LA-UR-21-29078

Approved for public release; distribution is unlimited.

Title:	Recent Advancements in Tools and Techniques for Materials Characterization in the EML
Author(s):	Schneider, Matthew M.
Intended for:	Talk for internal audience (possible external participants present).
Issued:	2021-09-15

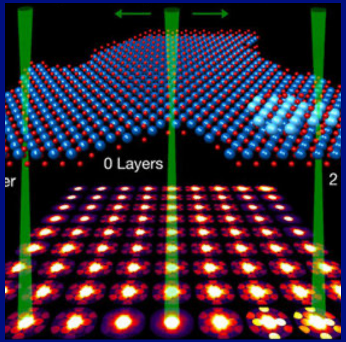
Los Alamos
NATIONAL LABORATORY

Recent Advancements in Tools and Techniques for Materials Characterization in the EML

Matt Schneider, MST-8

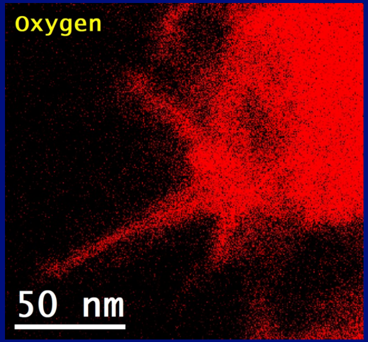
July 27th, 2021

Outline



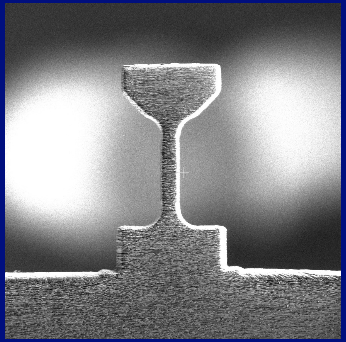
1. TEM: 4D-STEM

- High-spatial resolution
- Complicated & rich diffraction dataset



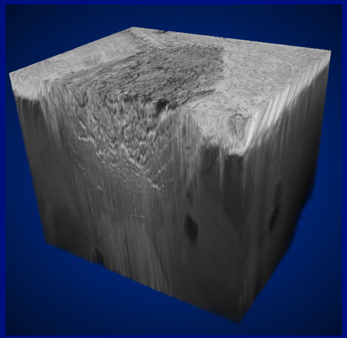
2. TEM: STEM-XEDS

- Rapid, high-spatial resolution chemical species mapping



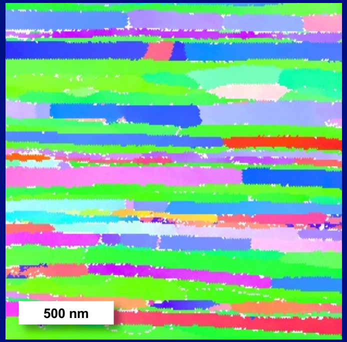
3. PFIB: µ-machining

- Large-scale, *in situ* micro-mechanical testing
- Prep for beamline experiments



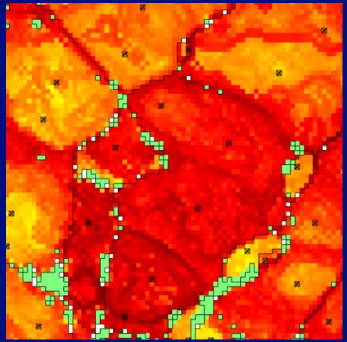
4. PFIB: 3D Datasets

- Imaging, chemical species mapping, and crystallography in 3D



5. SEM: TKD

- High-spatial resolution crystallography without TEM

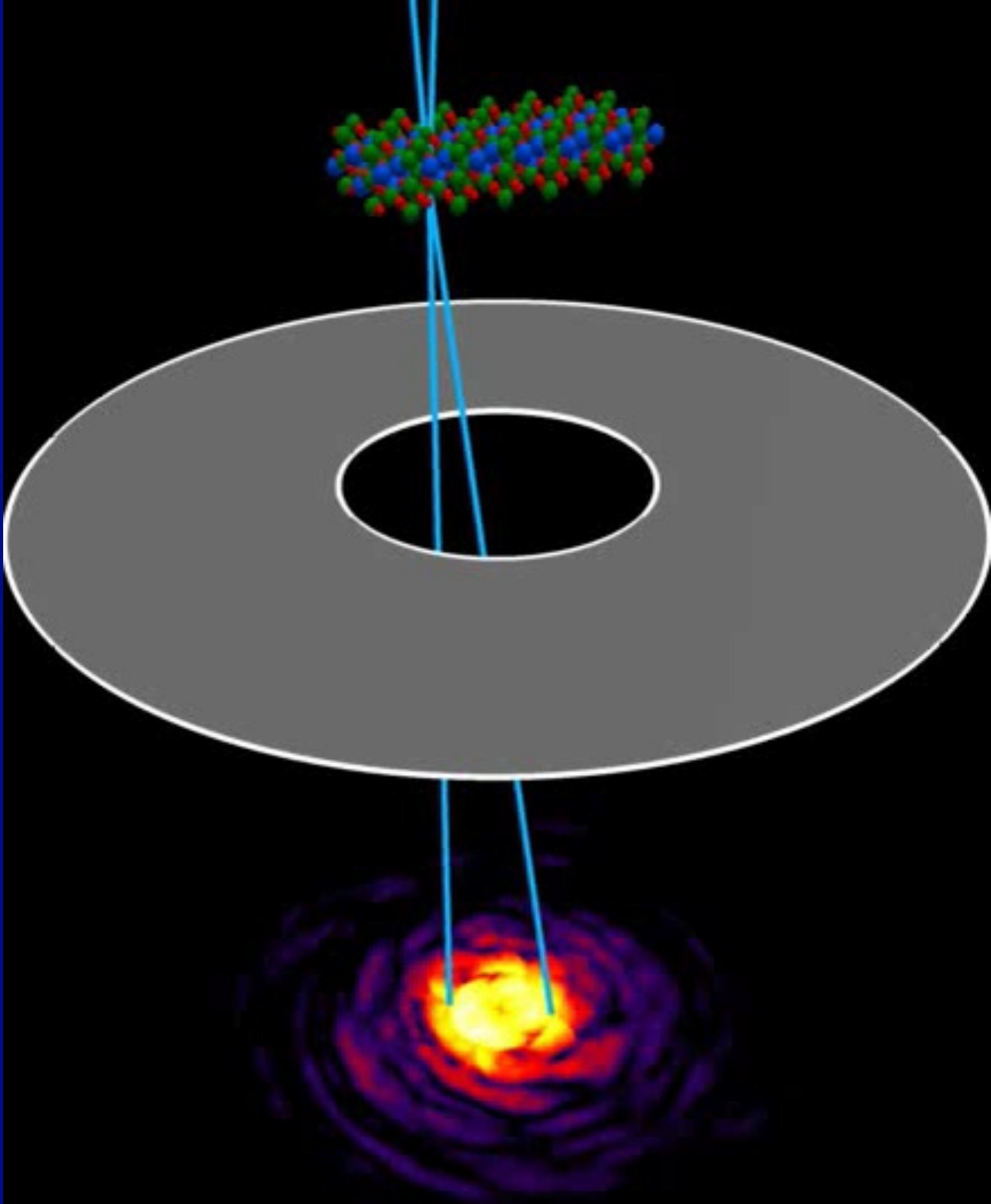


6. SEM: HR-EBSD

- High-angular resolution crystallographic data

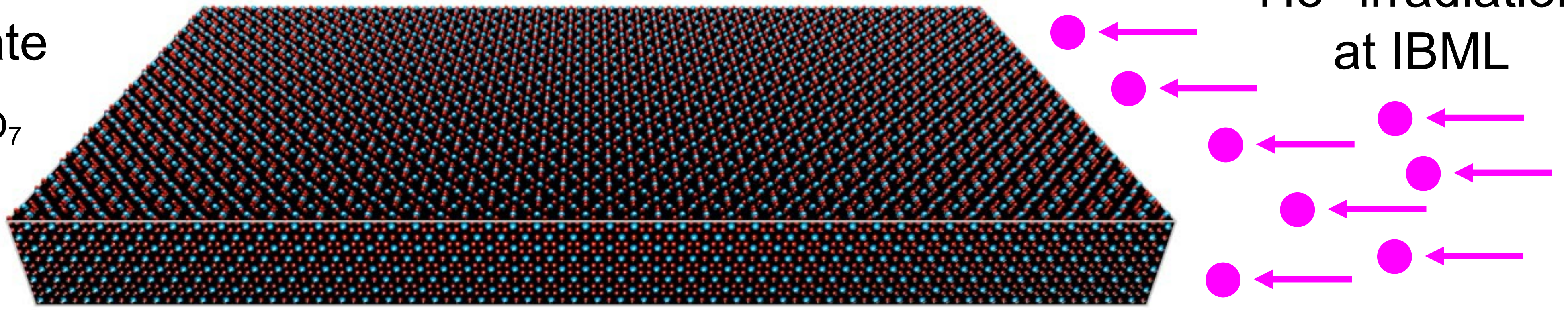
1. TEM: 4D-STEM

- Scanned electron probe
- Optics dictates a need to balance real- vs. reciprocal-space resolutions
- Real- & reciprocal-spaces, collected simultaneously → four dimensions
- Comparison of detection between 4D-STEM and traditional dark-field imaging
- Data sets are large (10's to 100's of GBs)



C. Ophus, Microscopy and Microanalysis 25, 563 (2019).

1. 4D-STEM: *In situ* Experiment – Complex Structural Analysis



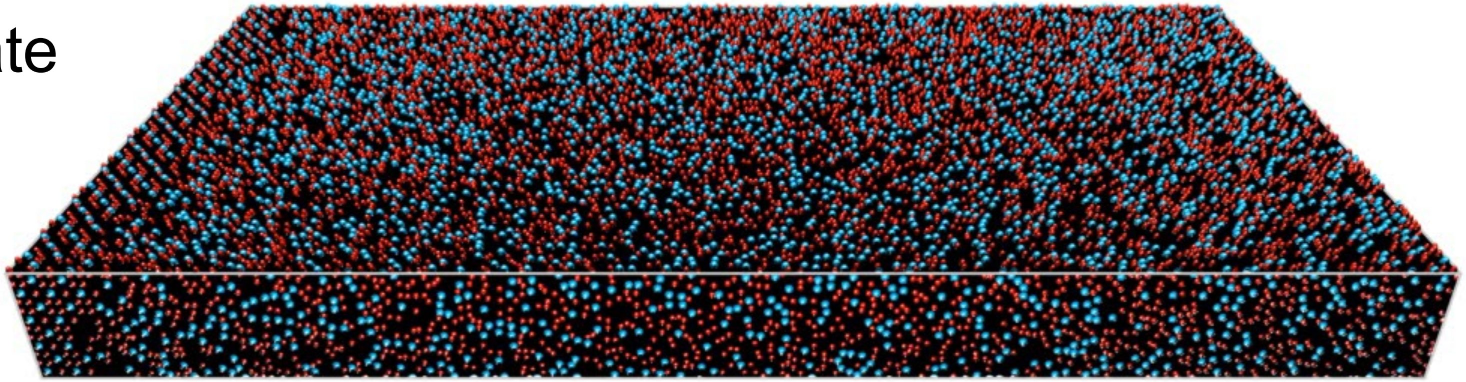
Gadolinium Titanate

- Composition: $Gd_2Ti_2O_7$
- Single crystal
- Pyrochlore structure
- 190 keV helium ions
- Nominal fluence of 10^{17} ions/ cm2
- Sample amorphized to a depth of ~1 µm
- He bubbles also present

Ref: B. Savitzky *et al.*, Microscopy and Microanalysis (2021).
LANL Collaborators: M. Janish, B. Derby

1. 4D-STEM: *In situ* Experiment – Complex Structural Analysis

Gadolinium Titanate

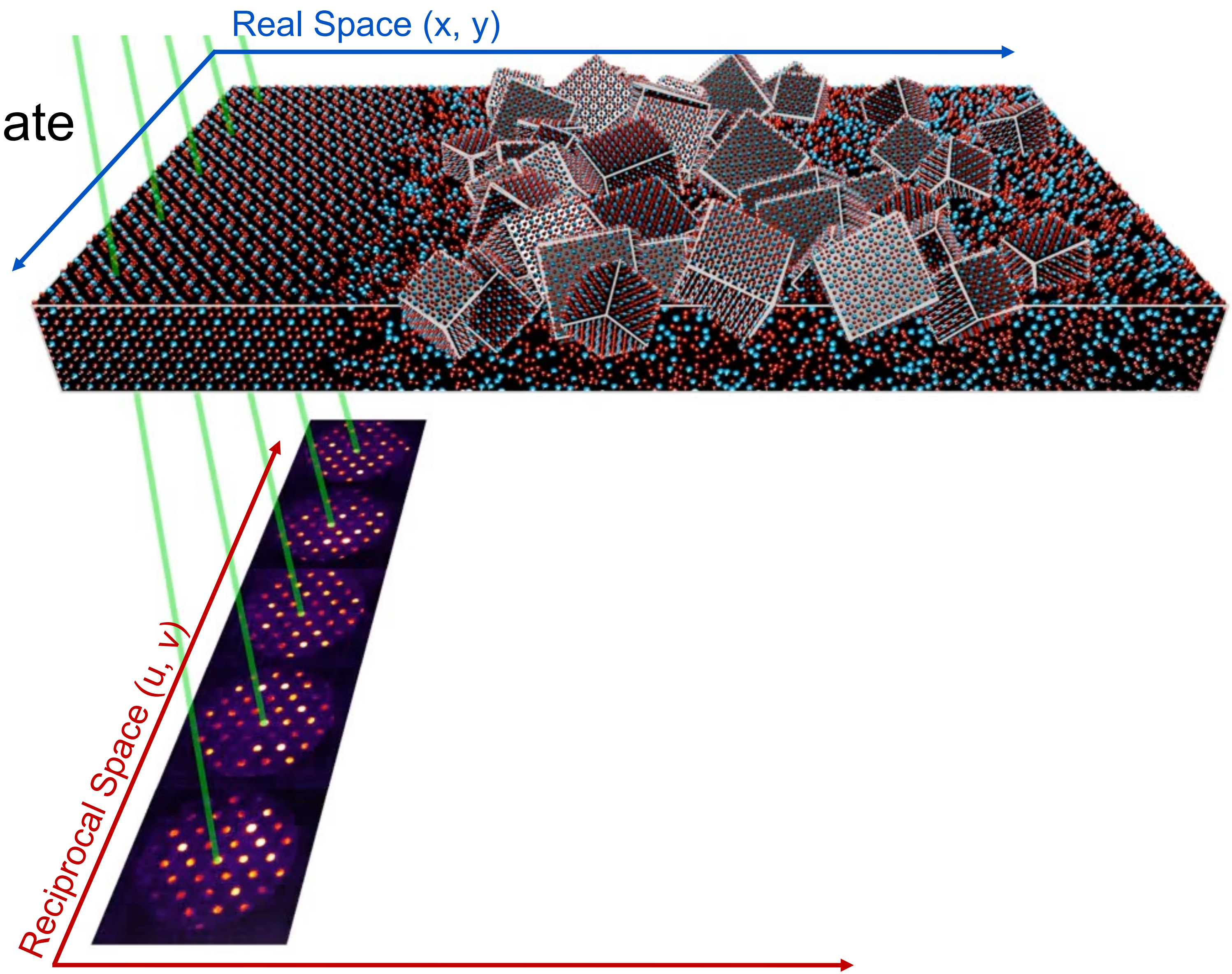


in situ
Annealing

Ref: B. Savitzky *et al.*, Microscopy and Microanalysis (2021).
LANL Collaborators: M. Janish, B. Derby

1. 4D-STEM: *In situ* Experiment – Complex Structural Analysis

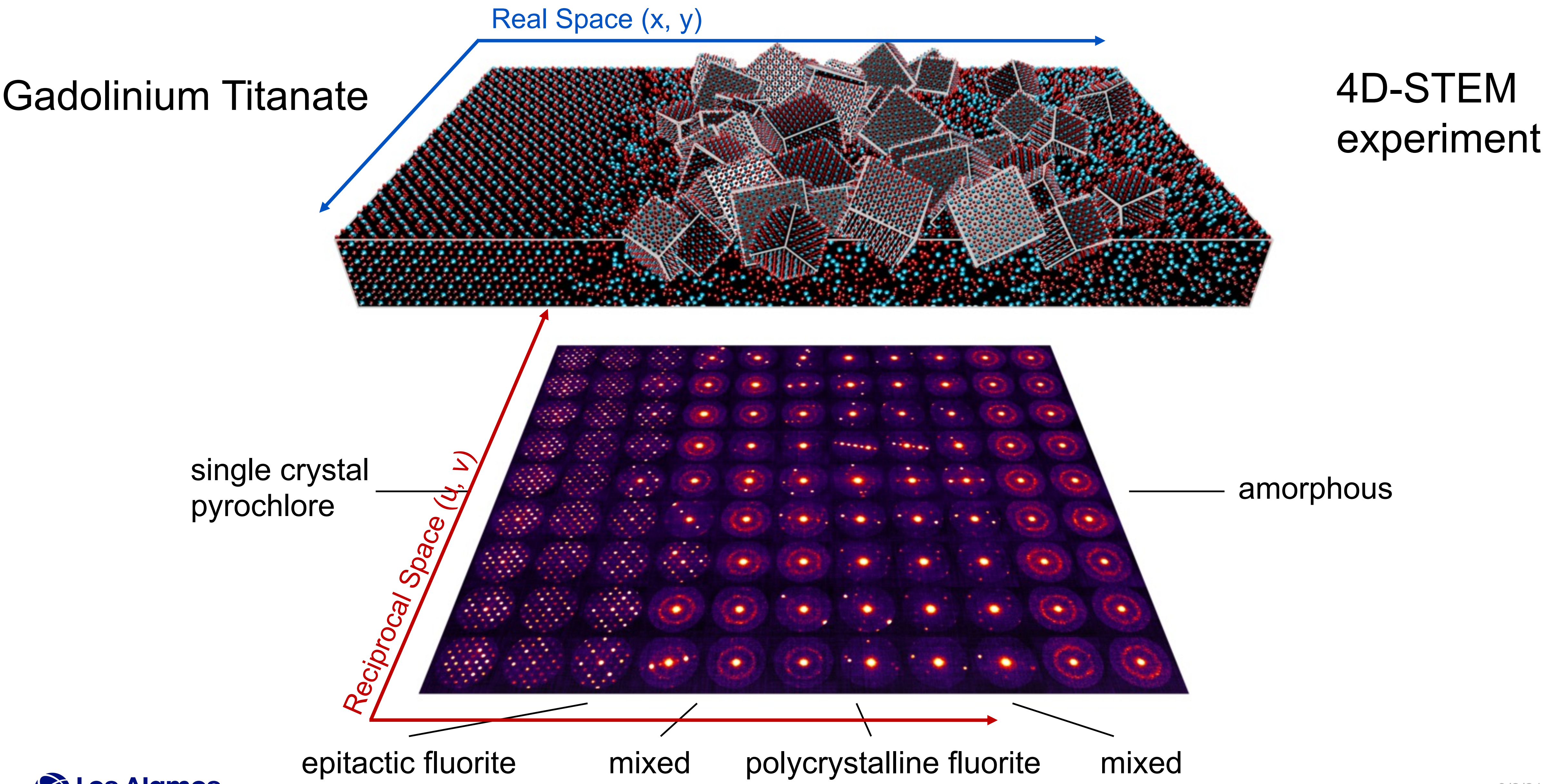
Gadolinium Titanate



4D-STEM experiment

Ref: B. Savitzky *et al.*, Microscopy and Microanalysis (2021).
LANL Collaborators: M. Janish, B. Derby

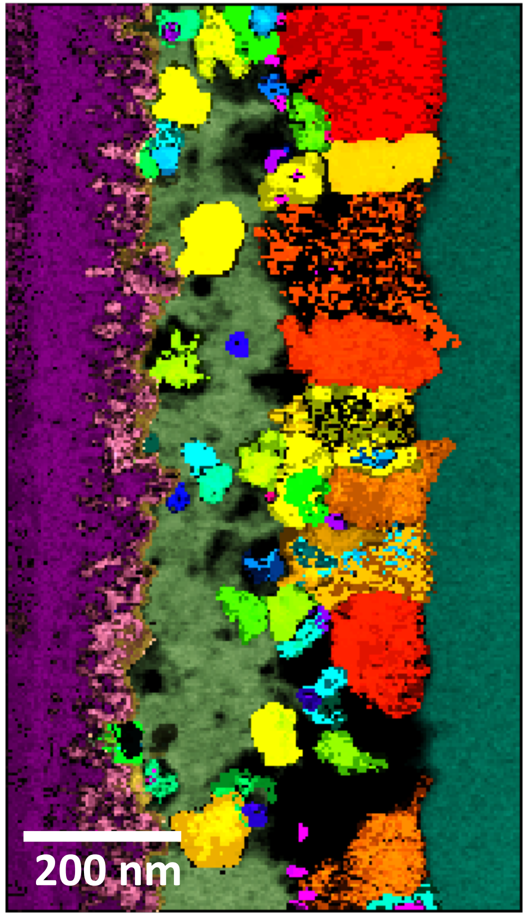
1. 4D-STEM: *In situ* Experiment – Complex Structural Analysis

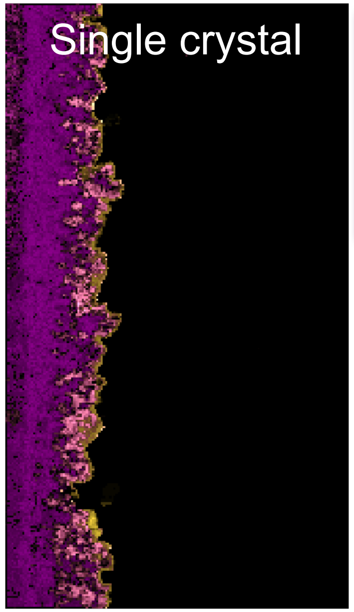


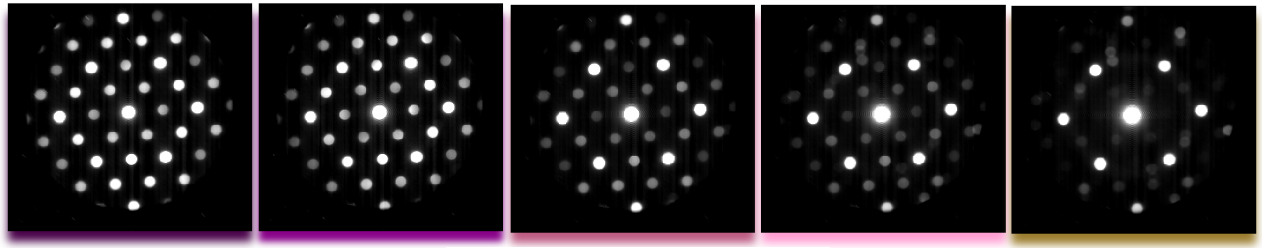
Ref: B. Savitzky *et al.*, Microscopy and Microanalysis (2021).

1. 4D-STEM: Data Analysis – Classification and Segmentation

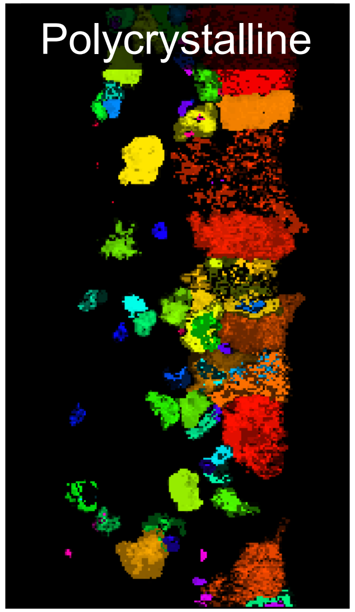
Classification applied to the GTO sample:

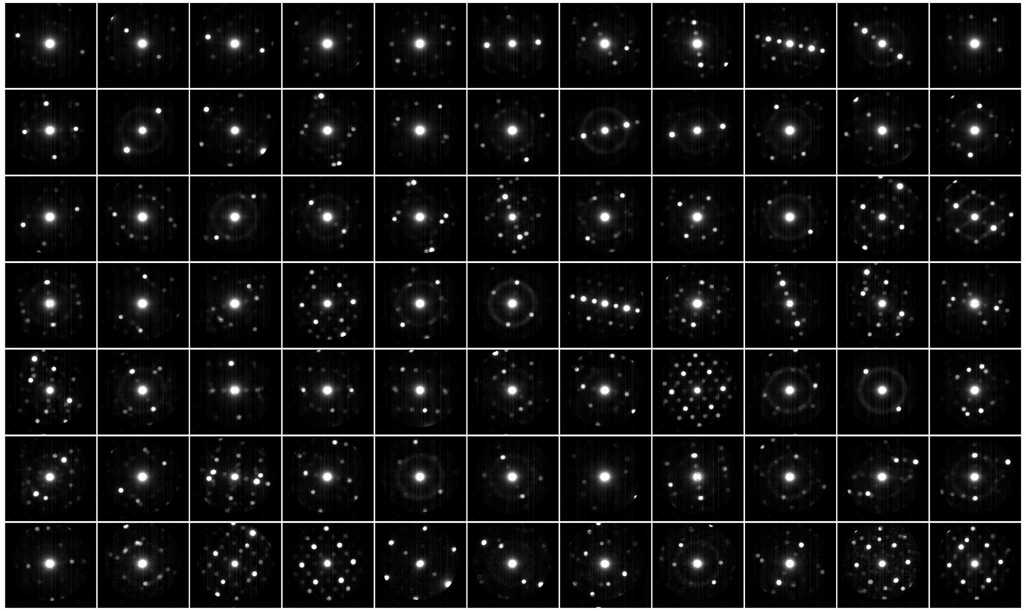


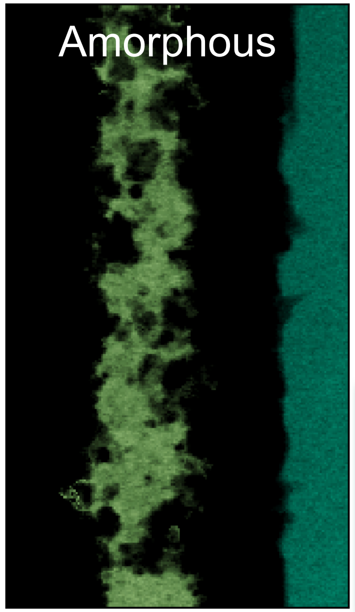


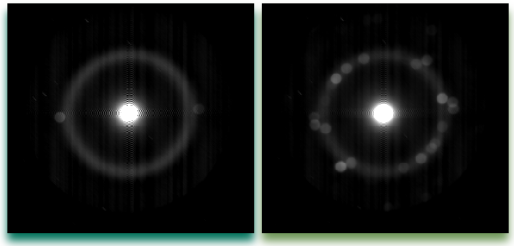


Decreased cation ordering







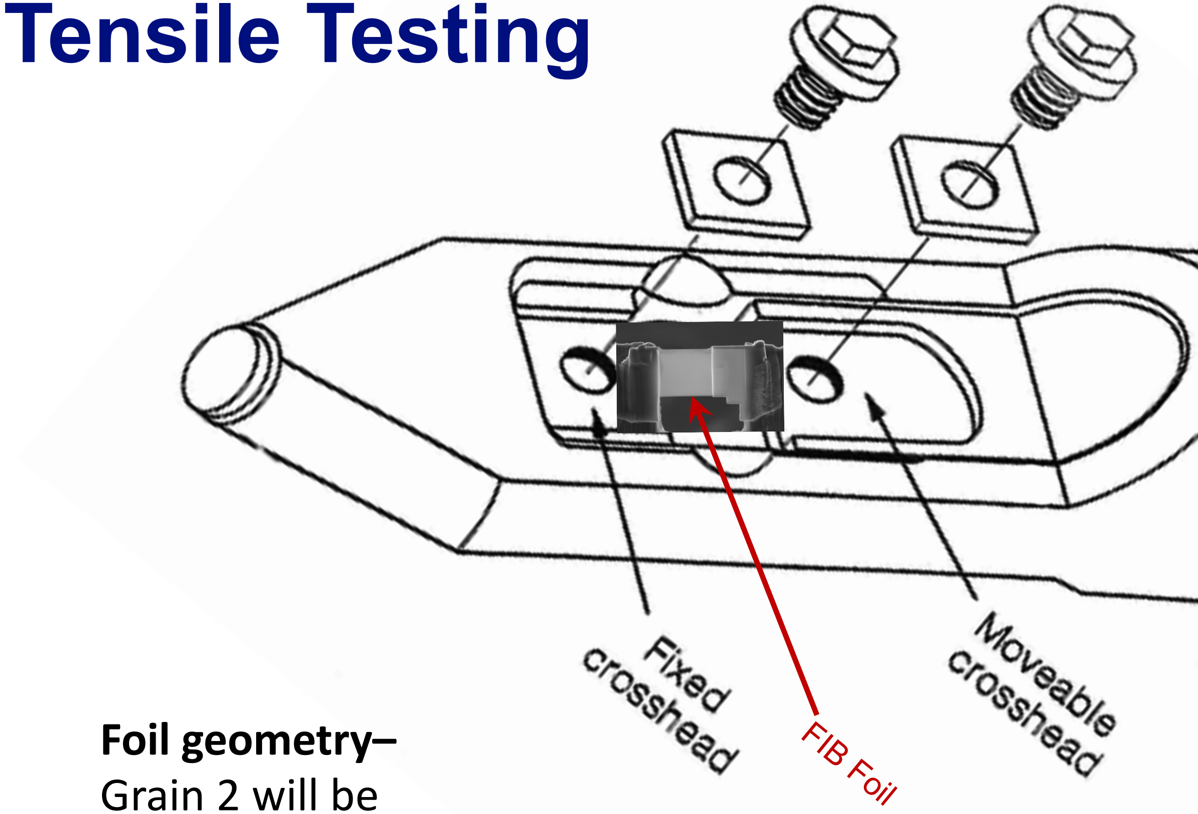


General classification is performed by disc registration and Bragg peak position classification. Implementation of full orientation mapping is underway.

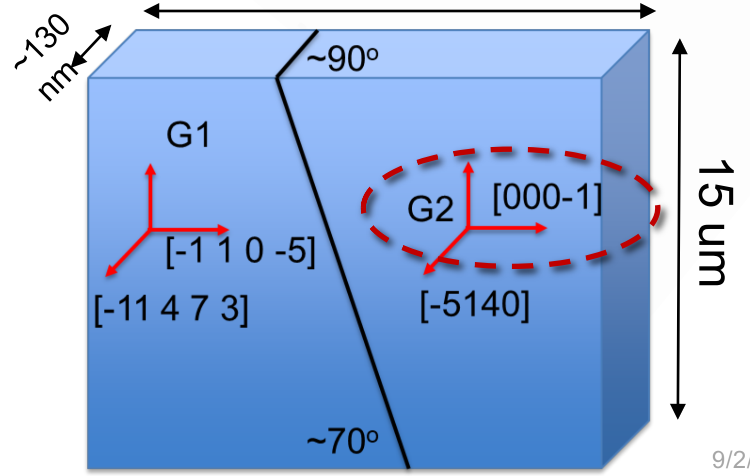
Ref: B. Savitzky *et al*., Microscopy and Microanalysis (2021).

1. 4D-STEM: *In situ* Experiment – Tensile Testing

- *In situ* tensile holder allows uniaxial tension to be applied to a TEM sample
- Prior characterization via electron back scatter diffraction (EBSD) allows specified tensile directions to be selected
- FIB sample prep ensures targeted orientation(s) are in the electron transparent region
- Hoping/expecting to observe twin formation in one or both grains
  - Primary goal was to capture the strain-field surrounding the twin tip before it interacts with a boundary



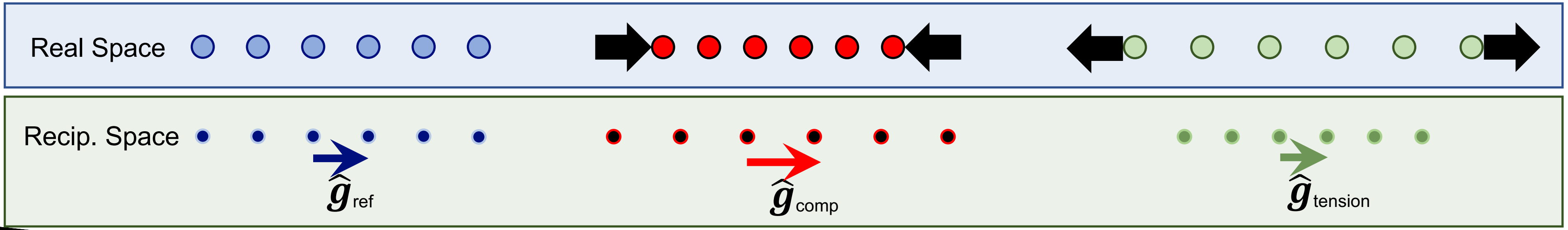
Foil geometry– Grain 2 will be in c-axis tension

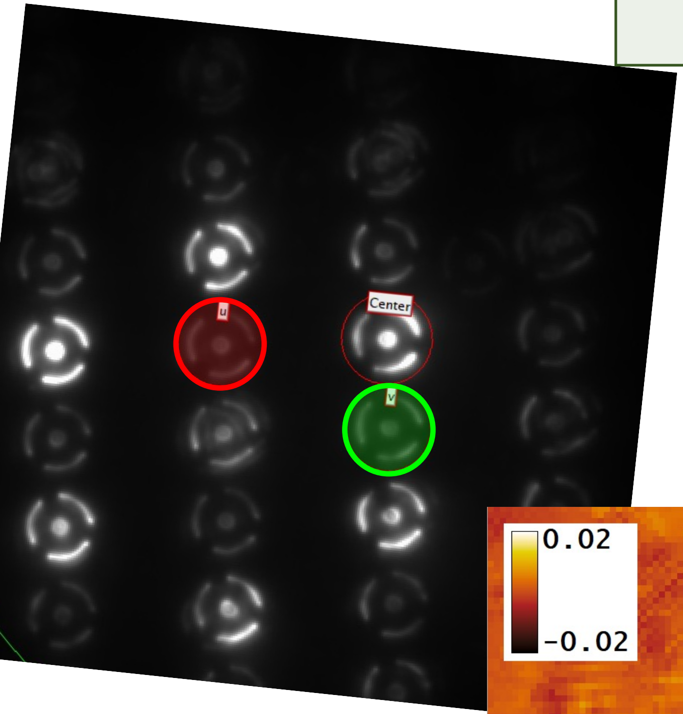


Collaborators: H. Vo, R. McCabe

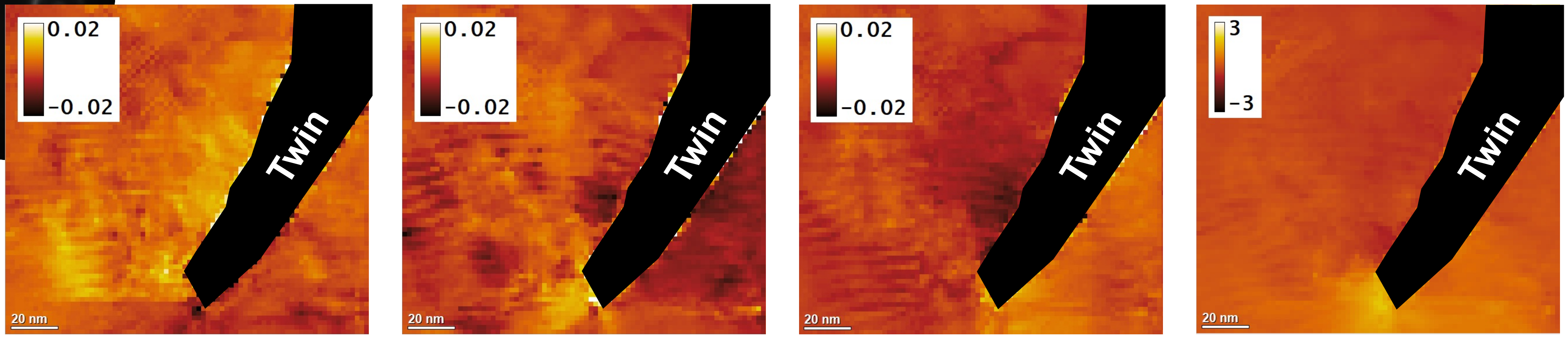
1. 4D-STEM: Data Analysis – Strain Mapping

$$\varepsilon = \frac{\hat{g}_{\mathrm{ref}} - \hat{g}_{\mathrm{strain}}}{\hat{g}_{\mathrm{ref}}}$$





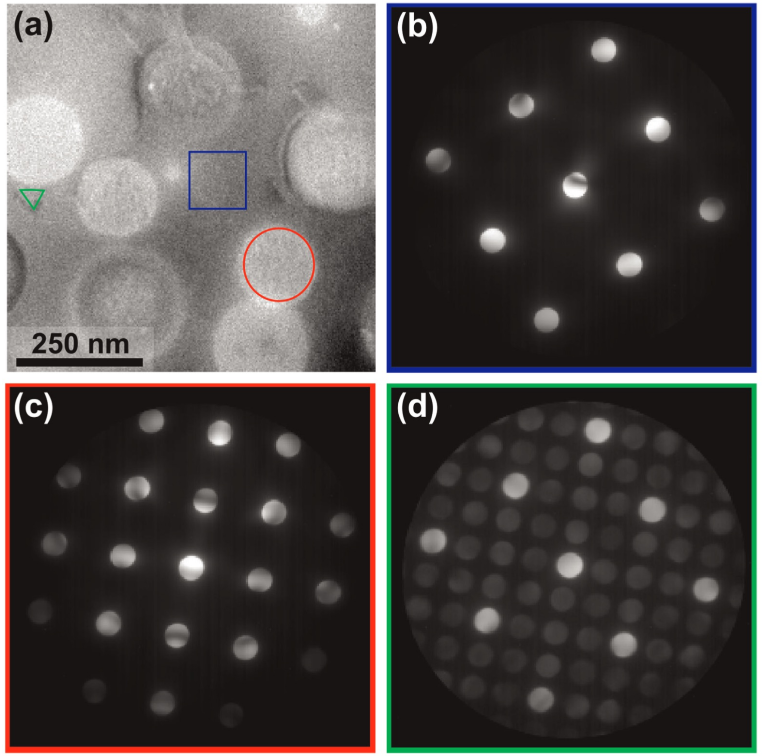
- Cross-, phase-, or hybrid-correlation used to measure shifts in Bragg peaks to sub-pixel precision; patterned probes used to increase precision of Bragg peak localization
- Strain maps computed by comparing location of Bragg peaks at each real-space pixel to reference pattern



ε_{xx} ε_{yy} ε_{xy} Rot

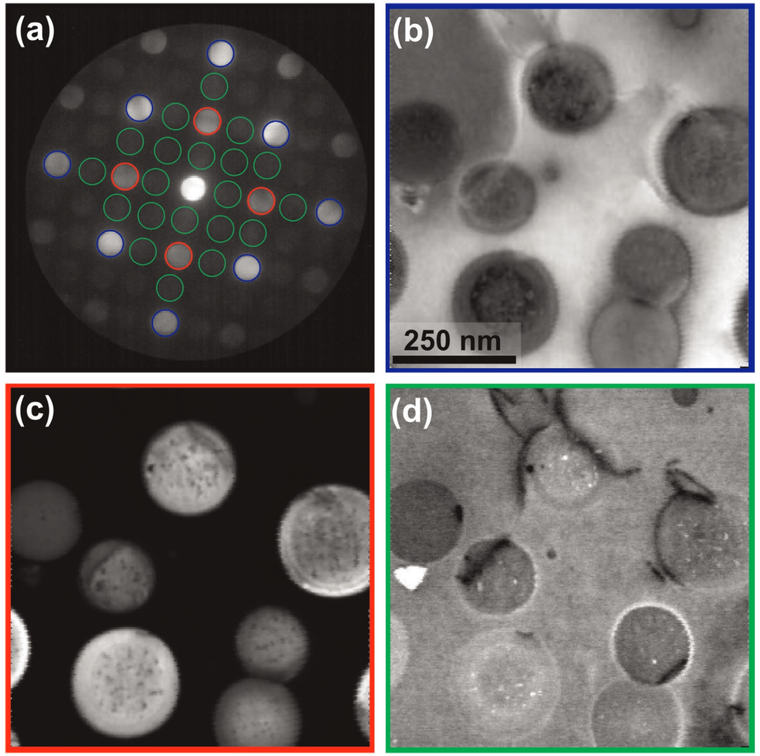
1. 4D-STEM: Data Cube Analysis – Virtual Detectors

- Fe–Al–Ni–Cr alloy
  - Matrix: BCC
  - Precipitates:
    - Coherent B2 NiAl
    - Coherent $Fe_{23}Zr_6$
- Work in real-space and extract reciprocal space data or vice/versa
- Virtual apertures are infinitely configurable
  - Arbitrary shaped virtual detectors possible
  - Extracted real-space images update in real-time



Navigate in real-space: extract diffraction patterns

- Rapid identification of several types of precipitates

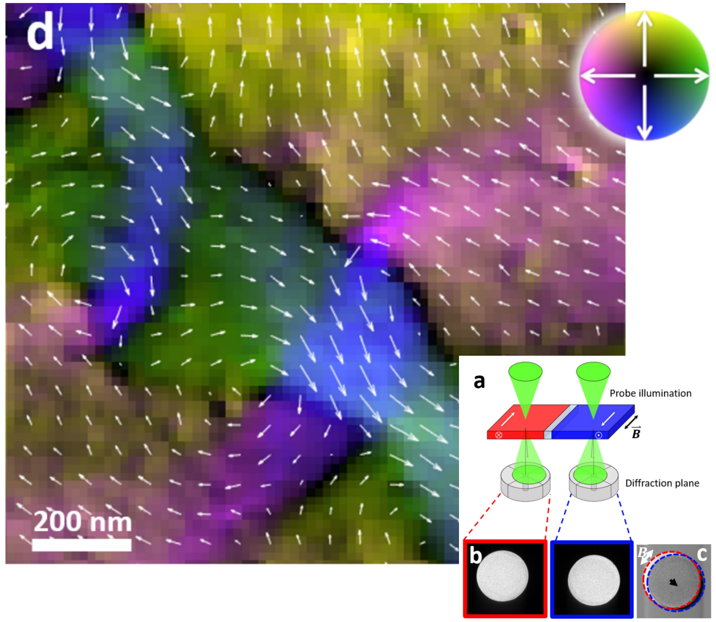


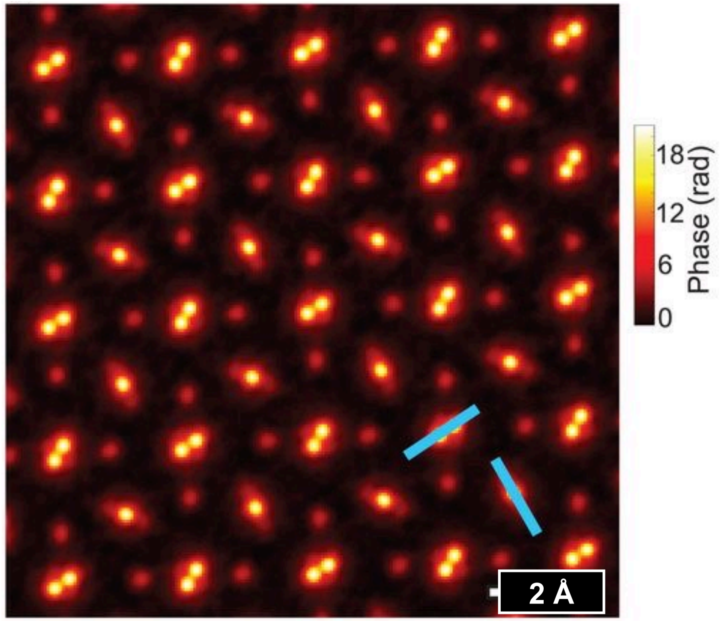
Navigate in reciprocal-space: Extract bright/dark-field images

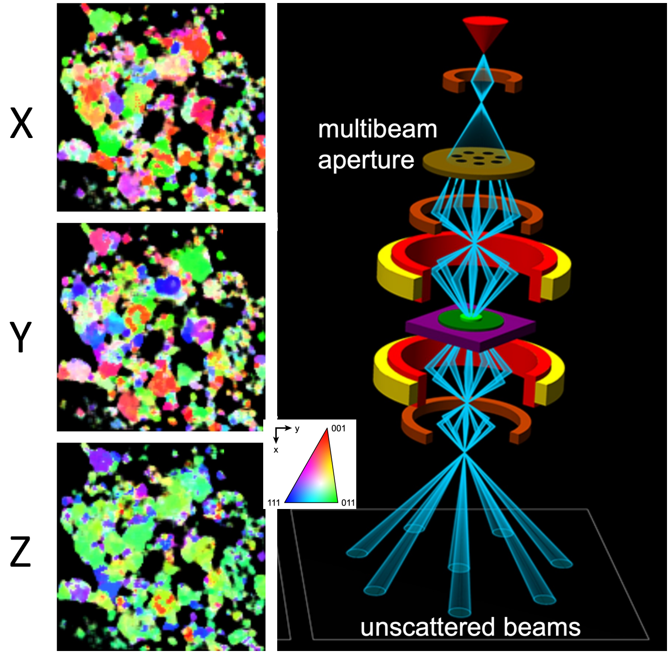
- Readily generate statistics on various phase volume fractions

Ref: C. Gammer *et al*., Ultramicroscopy 15, 1 (2015).

1. 4D-STEM: Many Other Applications in Development







STEM DPC

- Differential phase contrast measures deviations in position of center of mass of un-diffracted disc.
- Reconstruct sample's electrostatic or magnetic fields based on the displacement vector at each location in real-space

Kübel Group, Karlsruhe Institute of Technology

Electron Ptychography

- Coherent diffraction imaging method enables super-resolution
- Demonstrated resolution of ~0.2 Å, resolution limited by vibration of atoms, not by optics
- Limited to samples <30 nm thick

Z. Chen, Science 372, 826 (2021).

Multi-beam ACOM

- Specially constructed condenser aperture used to generate a circular array of electron beams
- Optics setup to focus all beams to single point on the sample
- Off-axis beams are able to access required HOLZ information

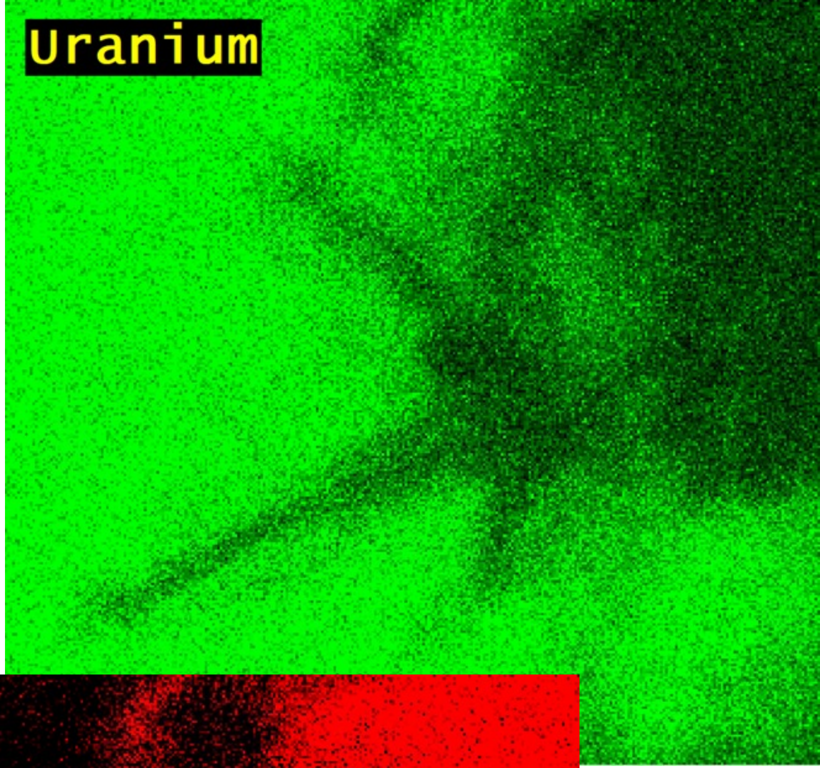
X. Hong, Microscopy & Microanalysis 27, 129 (2020).

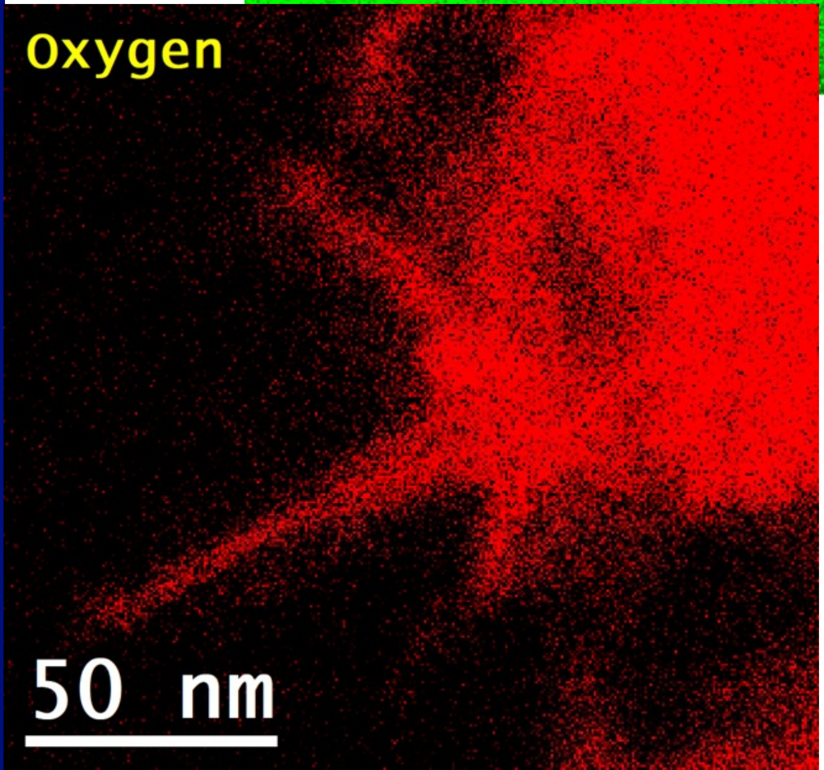
1. 4D-STEM: Technique's Current Status at the EML

- Status: Ready for use
  - Hardware fully integrated with the Titan S/TEM
  - Several users already trained and collecting datasets each week
- Challenges: Significant, but mostly manageable
  - Datasets can be 10's – 100's of GBs
  - Processing requires efficiently coded software running on computers with significant computational and memory resources
  - Code for very limited types of analyses available at the moment
- Prospects for future development: Excellent
  - Datasets contain far more information than current analysis codes are able to efficiently extract
  - Dynamical diffraction datasets require complex considerations, but contain a massive wealth of information
  - Multi-beam ACOM collaboration with NCEM just getting going, hope to have beta-implementation operational within 1 calendar year

2. TEM: STEM-XEDS

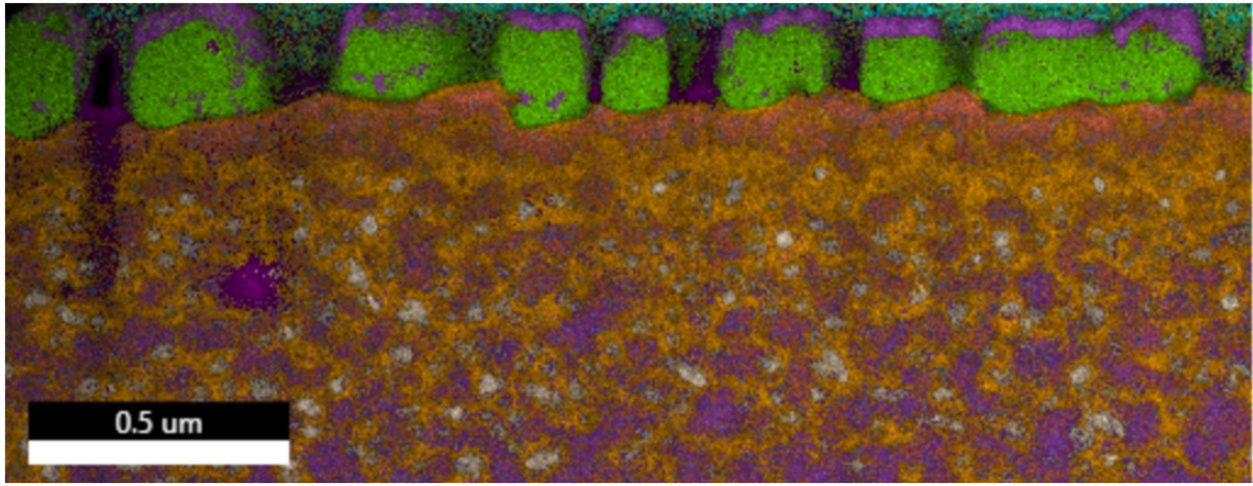
- Scanned transmission electron probe
- 300 kV primary electrons interact with sample to produce x-rays with a spectrum of wavelengths/energies
- X-ray energy-dispersive spectroscopy (XEDS) analyzes the energies of these x-rays and correlates them back to electronic structures characteristic of each element





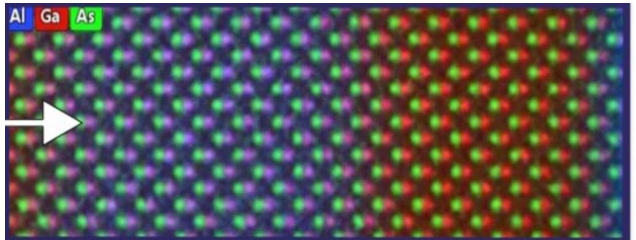
2. XEDS: New Silicon-Drift Detector on Titan

- XEDS detector upgraded from 30 mm^2 to 70 mm^2 active-area sensor
- Collection angle has gone from <0.1 sr to >0.45 sr collection angle
- >200 kcps throughput
  - High-quality mapping now possible in short time-frames (5-20 minutes)
- Spatial resolution limits in TEM determined by optics (not beam broadening)
  - Titan limited to 1.36Å at the extreme, in practice 1 nm is easy.



- Sample:
  - Approximately equiatomic Fe-Mn-Cr-Ni HEA
  - Phase segregated due to 400 DPA irradiation

9% C K
13% O K
14% CrK
21% MnK
17% FeK
2% CoK
19% NiK
4% CuK
1% GaK



HEA sample courtesy of J. Gigax

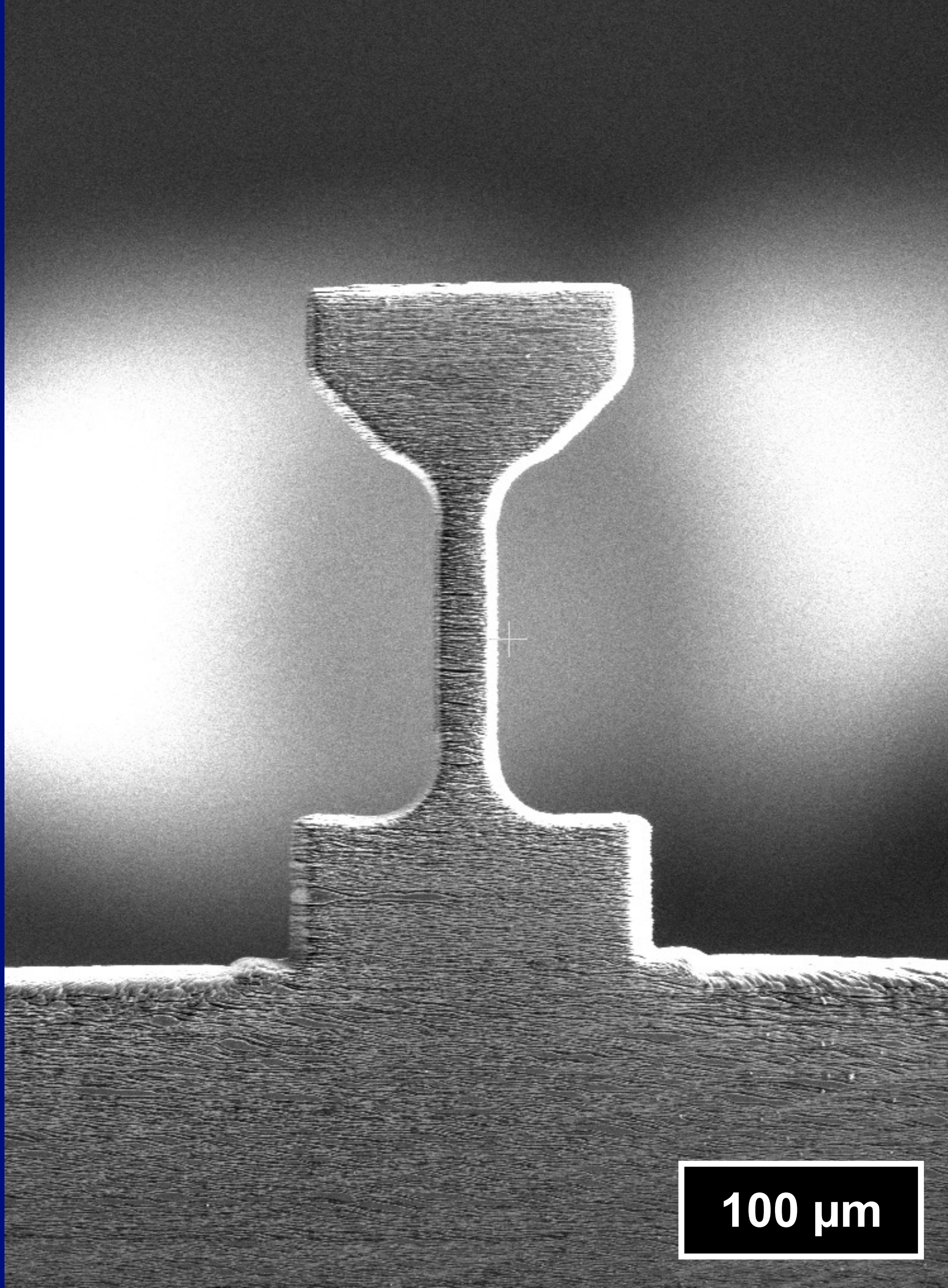
AlGaAs Image: ThermoFisher Scientific

2. XEDS: Technique's Current Status at the EML

- Status: Ready for use
  - Hardware fully integrated with the Titan S/TEM
- Challenges: Minor
  - Certain combinations of elements have spectral overlaps that can be challenging to resolve, an inherent limitation of XEDS
  - Highly accurate quantification requires use of known standards for proper calibration
  - Very high-quality, large-area maps require long mapping times
    - Unfortunately the room's temperature stability is currently the limiting factor
- Prospects for future development: Mature technology, usability improvements expected in software
  - Possibility of implementing Zeta-Factor-based quantification for improved standardless quantification
  - Ideally, EML would have database of standards available for common compounds to improve quantification results for user-base

3. Micromachining

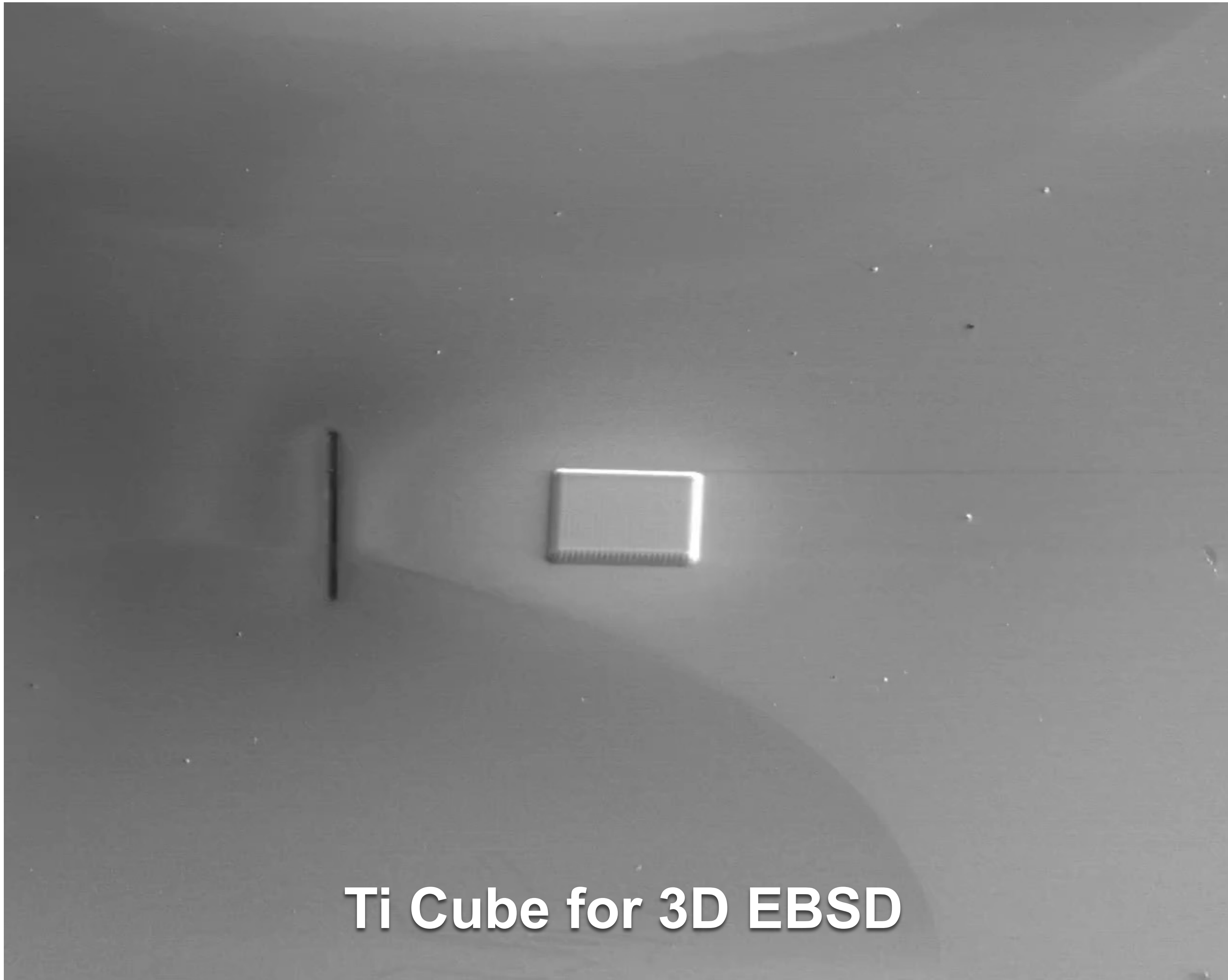
- Positively charged ions are focused with electro-magnetic lenses and steered across the sample surface
- Ions locally sputter wherever they impinge
  - Low beam currents used for imaging
  - High beam currents used for directed material removal
- Traditional FIB: Ga^{+} ions, beam current maxes out around 65 nA
- Plasma FIB: Xe^{+} ions, maximum beam current on EML instrumentation 2.5 μA



Los Alamos
NATIONAL LABORATORY

3. Micromachining: Rapid prep of large samples for 3D

- PFIB Ion beam currents of up to 2.5 μA greatly accelerate bulk material removal
  - Approximately 40 times faster than Ga^+ FIB
- In this video: 1 μA beam cleanly cuts bulk Ti
  - Minimal clean-up required
- 100 x 100 x 100 μm^3 cube fabricated in <4 hours



Los Alamos NATIONAL LABORATORY

Collaborators: R. McCabe

3. Micromachining: *in situ* micro-mechanical testing

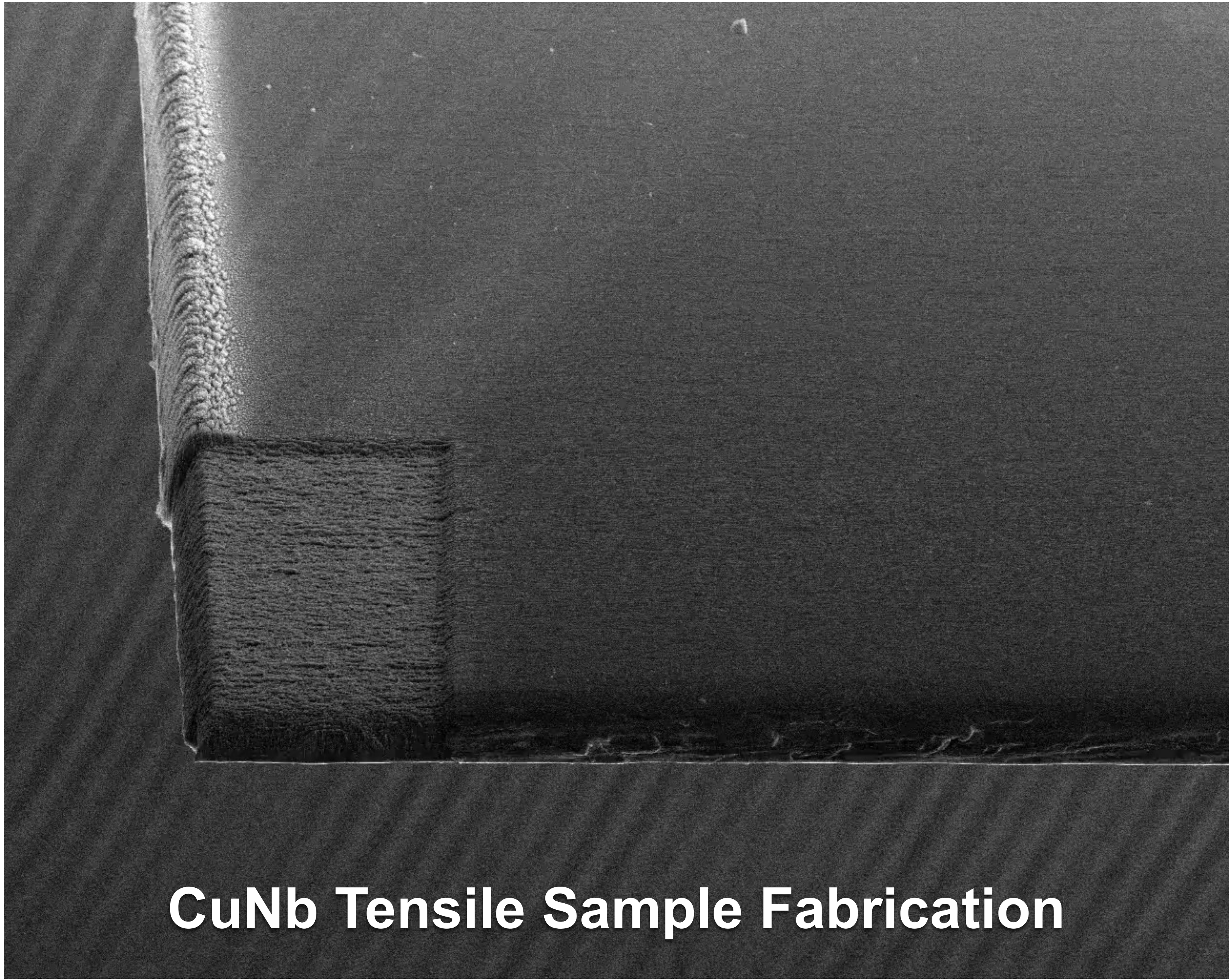
- Readily fabricate/modify test apparatus geometries for each experiment
- W blank cut out using CINT's FemtoScribe capability
- PFIB used for finer, cleaner finishing

Los Alamos NATIONAL LABORATORY

Collaborators: R. McCabe, Y. Zhang, N. Li, J. Gigax

3. Micromachining: *in situ* micro-mechanical testing

- Readily adapt test apparatus geometries to suit each experiment
- Rapid fabrication of meso-scale samples for mechanical testing

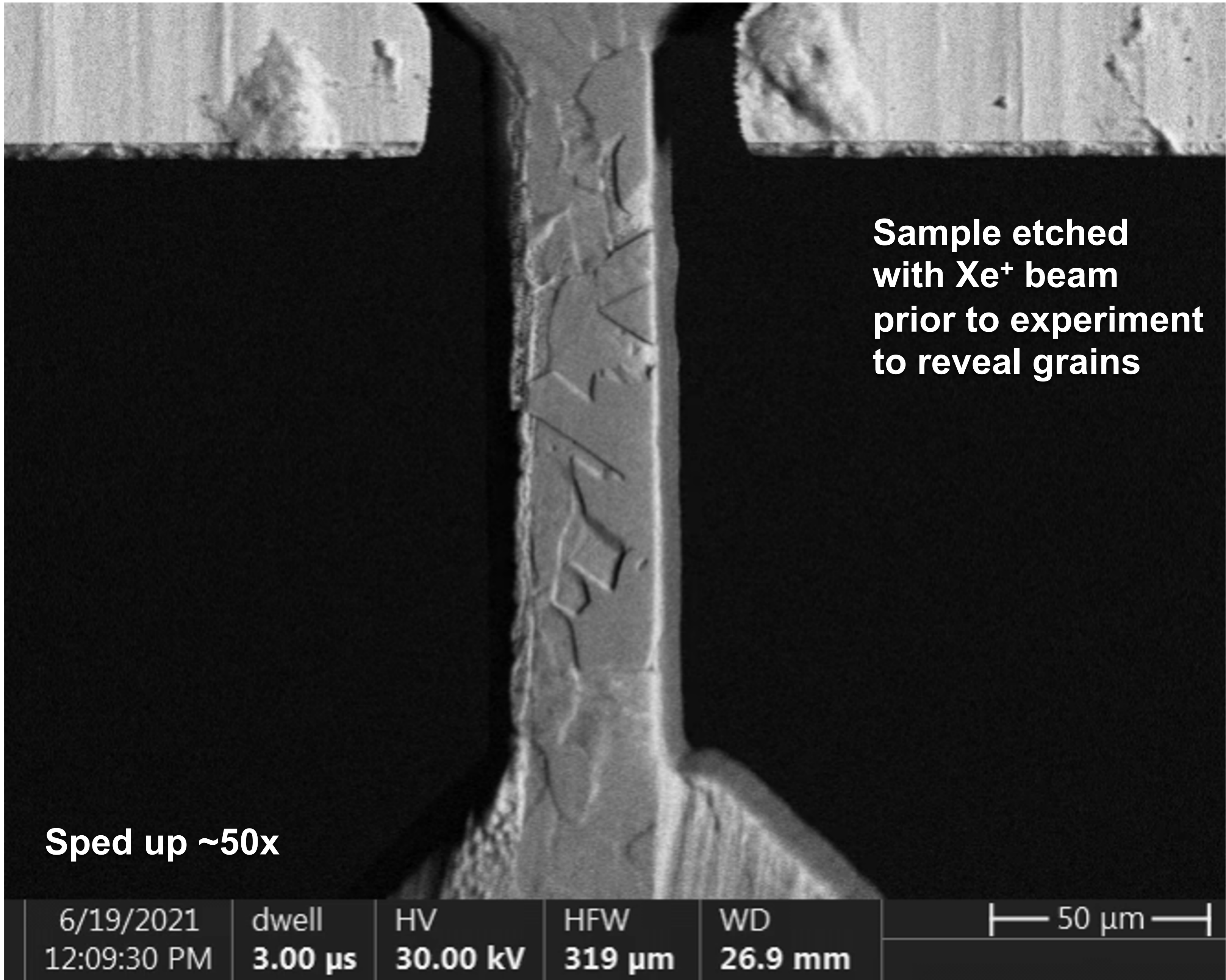


Los Alamos NATIONAL LABORATORY

Collaborators: R. McCabe, Y. Zhang, N. Li, J. Gigax

3. Micromachining: *in situ* micro-mechanical testing

- Readily adapt test geometries to customize experiment
- Rapid fabrication of meso-scale samples for mechanical testing
- Conduct testing *in situ*

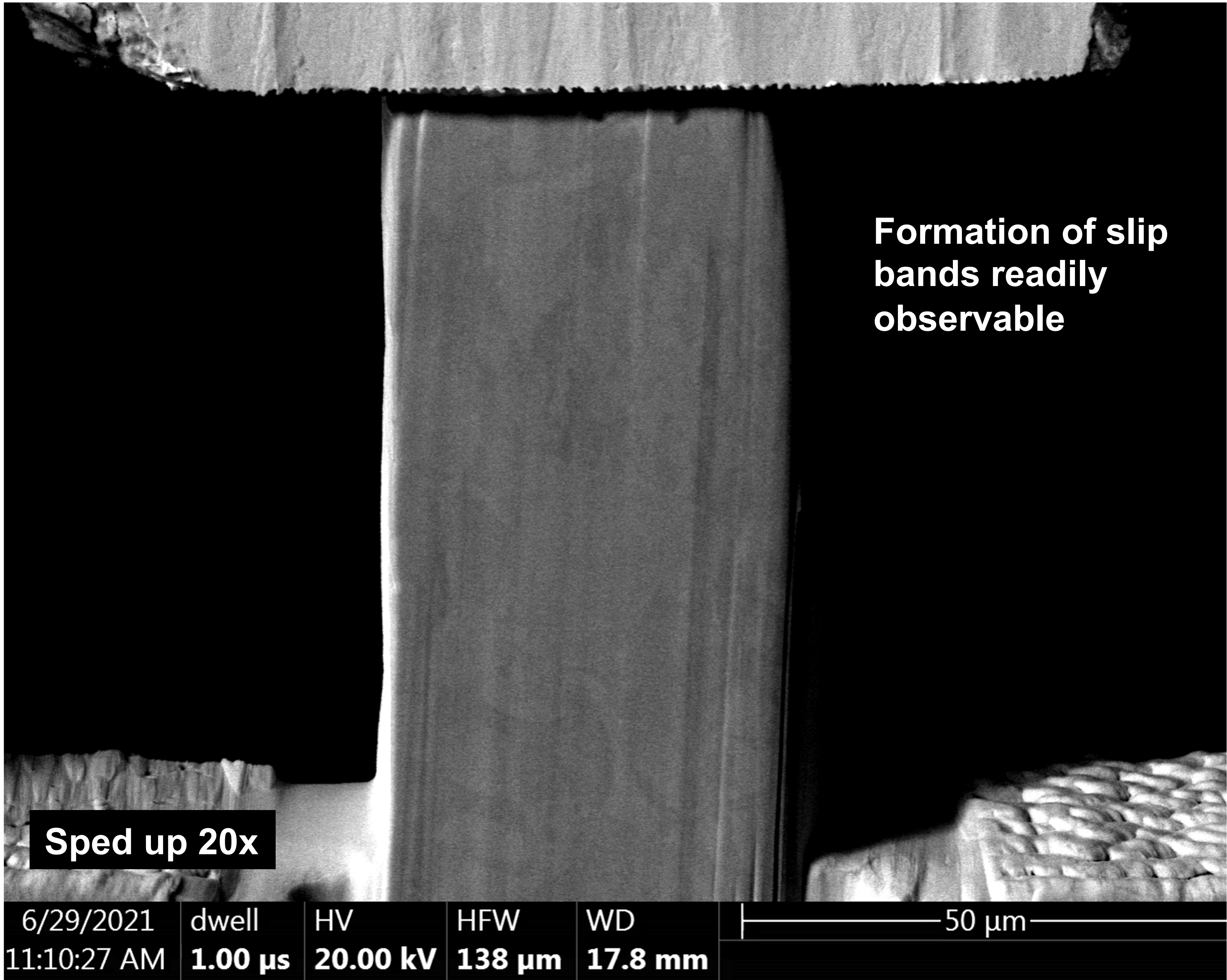


Los Alamos NATIONAL LABORATORY

Data courtesy of iMIDAS project [J. Gigax, N. Li, S. Fensin]

3. Micromachining: *in situ* micro-mechanical testing

- Readily adapt test geometries to customize experiment
- Rapid fabrication of meso-scale samples for mechanical testing
- Conduct testing *in situ*
  - Integrate analytical (*e.g.* EBSD) capabilities while testing
  - Entire process is *in situ*, air-sensitive samples are not a problem



Los Alamos NATIONAL LABORATORY

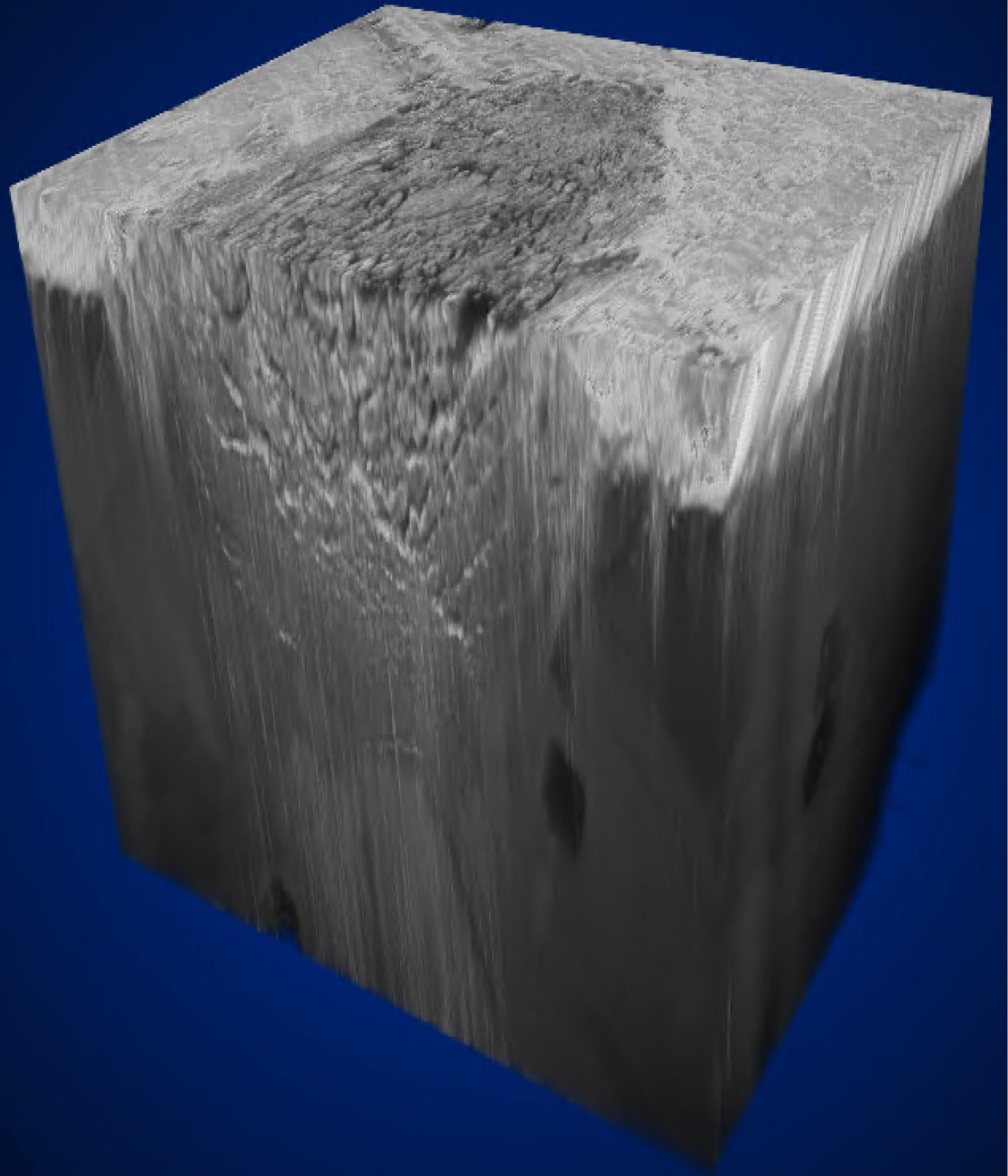
Data courtesy of iMIDAS project
[J. Gigax, N. Li, S. Fensin]

3. Micromachining: Technique's Current Status at the EML

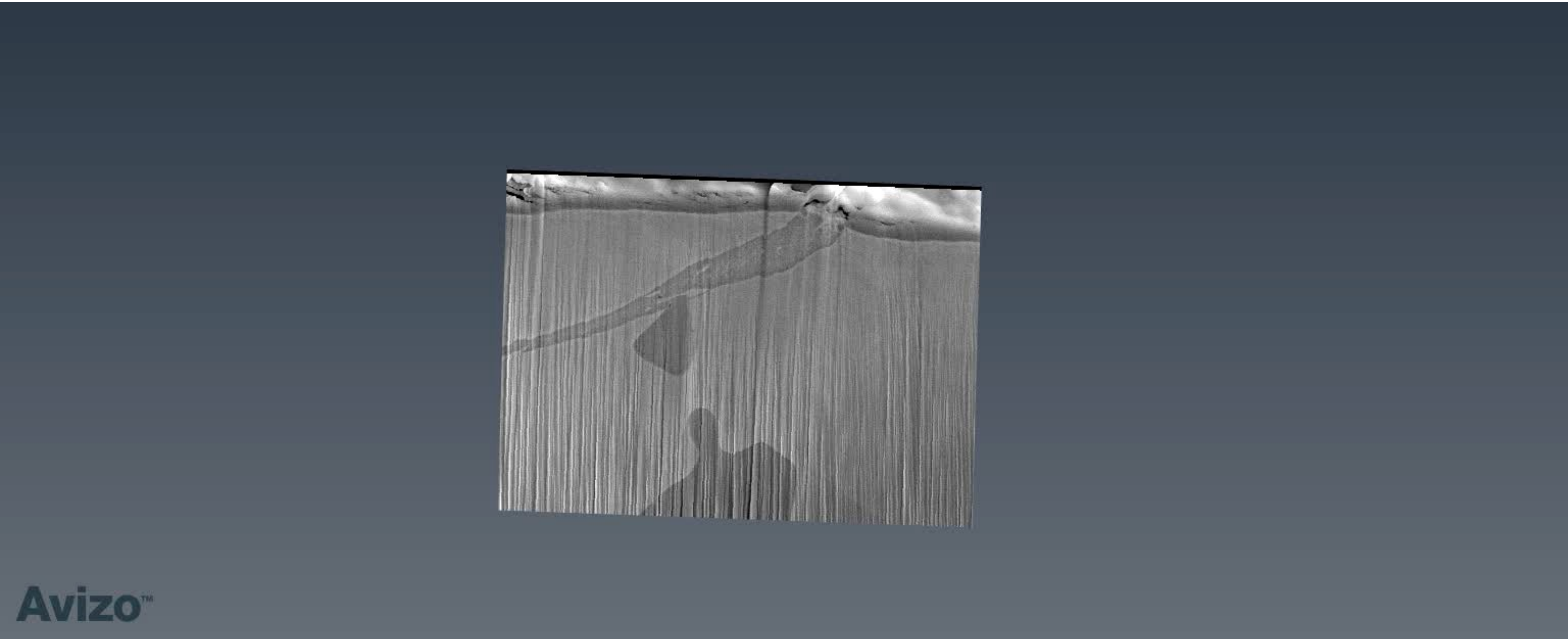
- Status: Almost ready for use
  - PFIB fully installed, most bugs worked out (very slow Xe gas leak being localized)
- Challenges: Minor?
  - In development phase of procedures for EML users, a few challenges have arisen but these are anticipated to be solvable in the near future
  - As always, *in situ* experiments require careful setup and data collection
- Prospects for future development: Excellent
  - LANL is ahead of the curve (though not leading, yet)
  - There is a large amount of materials science to be done between the Ga^+ FIB and the bulk sample regimes

4. PFIB: 3D Datasets

- Serial cross sectioning conducted by carefully milling away slices of a controlled thickness followed by the collection of secondary electron images and/or other signals of interest
- Datasets are reconstructed into 3D data-cubes that are directly interpretable



4. 3D Datasets: Serial Cross-Sectional Imaging

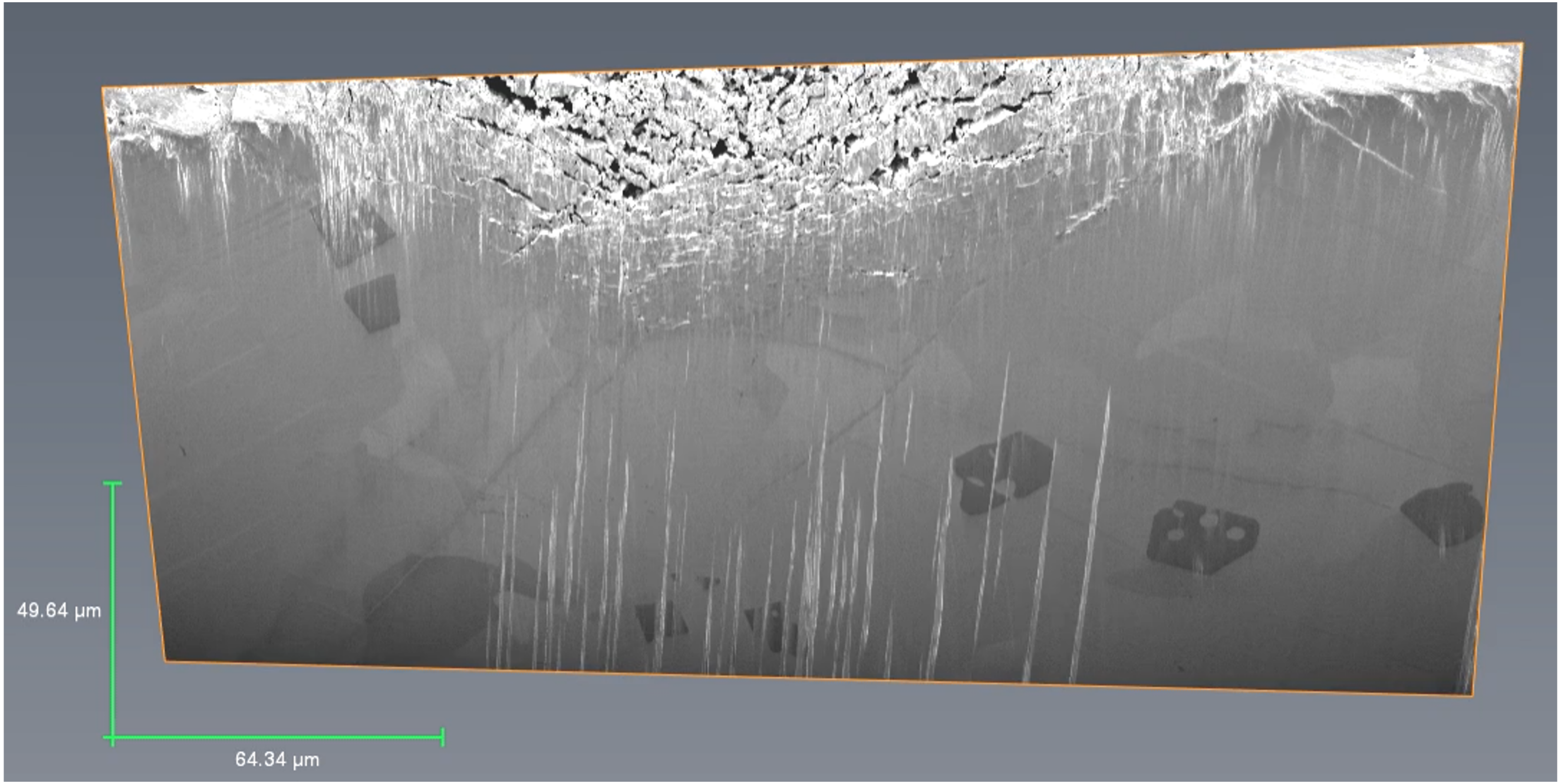


- Dataset dimensions: ~30 x 25 x 85 µm
- Collected on Ga+ FIB over ~24 hours
- Manually segmented over >40 hours (Thanks COVID-19!)

Collaborators: E. Tegtmeier, A. Richards

Los Alamos NATIONAL LABORATORY

4. 3D Datasets: Serial Cross-Sectional Imaging

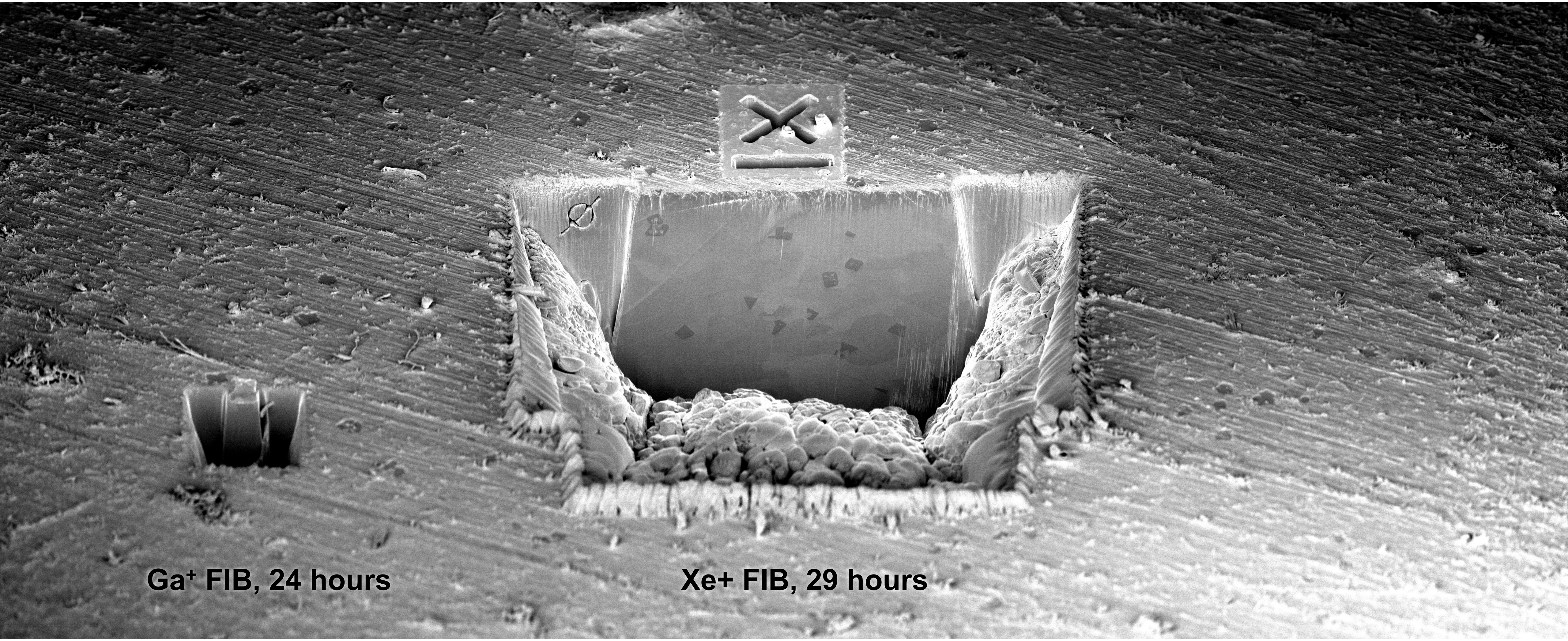


- Dataset dimensions: ~300 x 250 x 300 µm
- Collected on Xe+ FIB over ~28 hours
- Machine-learning based segmentation underway

Collaborators: E. Tegtmeier, A. Richards

Los Alamos NATIONAL LABORATORY

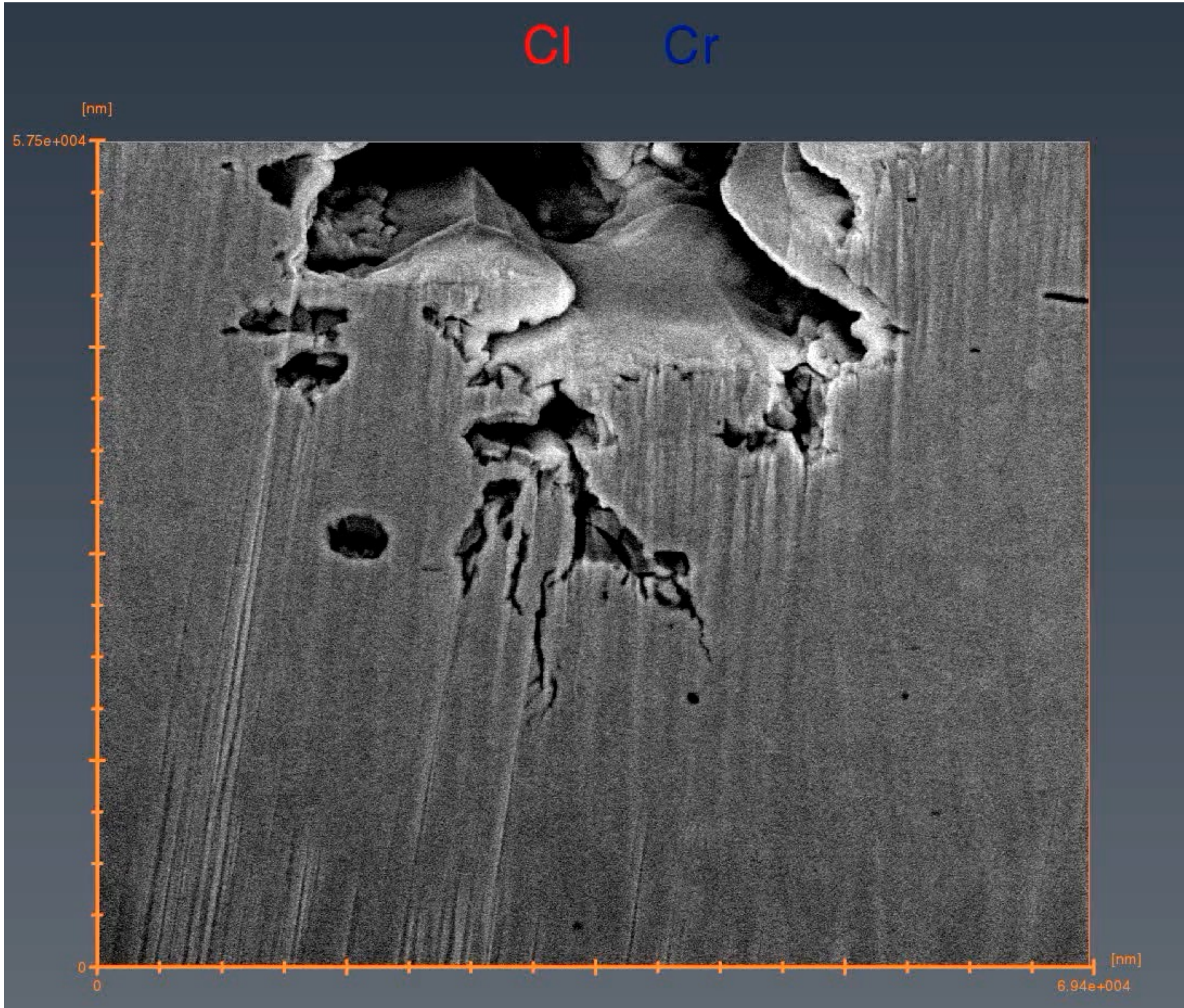
4. 3D Datasets: Serial Cross-Sectional Imaging



- PFIB investigates > 350x the volume in approximately the same amount of time
- Manual segmentation does not scale, ML required

4. 3D Datasets: Imaging + XEDS Mapping

- Sample: Stainless steel
  - Accelerated corrosion conducted with exposure to Cl gas
- Collection of XEDS maps, coupled with imaging enables a more complete understanding of spatial relationship between various phases



Data courtesy of E. Tegtmeier

4. 3D Datasets: 3D-EBSD

- 3D EBSD enables the study of relationships between grains in far greater detail than any single slice through a given material
- Sample: Titanium
  - 100 x 100 x 100 um^3
- Data collection details:
  - FIB slice time ~75 seconds
  - EBSD collection ~100 seconds
  - 250 nm cubic voxels (from 250 nm thick slices)
  - Sample prep to 3D EBSD data ~24 hours

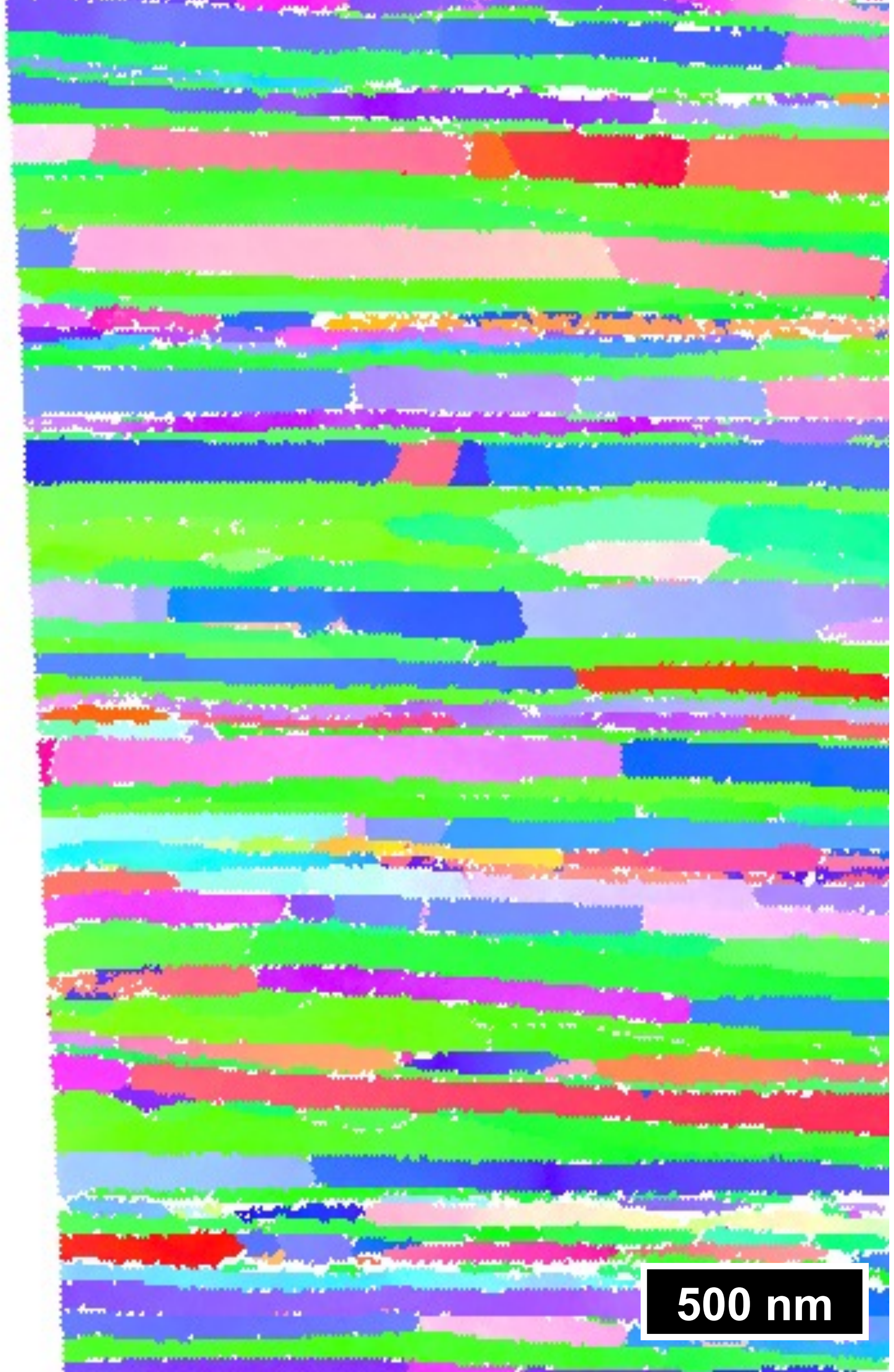
Collaborators: R. McCabe

4. 3D Datasets: Technique's Current Status at the EML

- Status: Almost ready for use
  - PFIB fully installed, most bugs worked out (very slow Xe gas leak being localized)
- Challenges: Minor?
  - In development phase of procedures for EML users, a few challenges have arisen but these are anticipated to be solvable in the near future
  - Optimization of data collection procedures underway, small gains per-frame save many hours over the entire process
- Prospects for future development: Excellent
  - LANL is ahead of the curve (though not leading, yet)
  - Three dimensional analyses are far more complete than single-frames
  - These datasets are useful inputs for modelling efforts at various length-scales
  - Prospects for machine-learning/AI based data analyses are quite positive and these techniques are absolutely needed to aid in processing the large volumes of data generated

5. SEM: Transmission Kikuchi Diffraction (TKD)

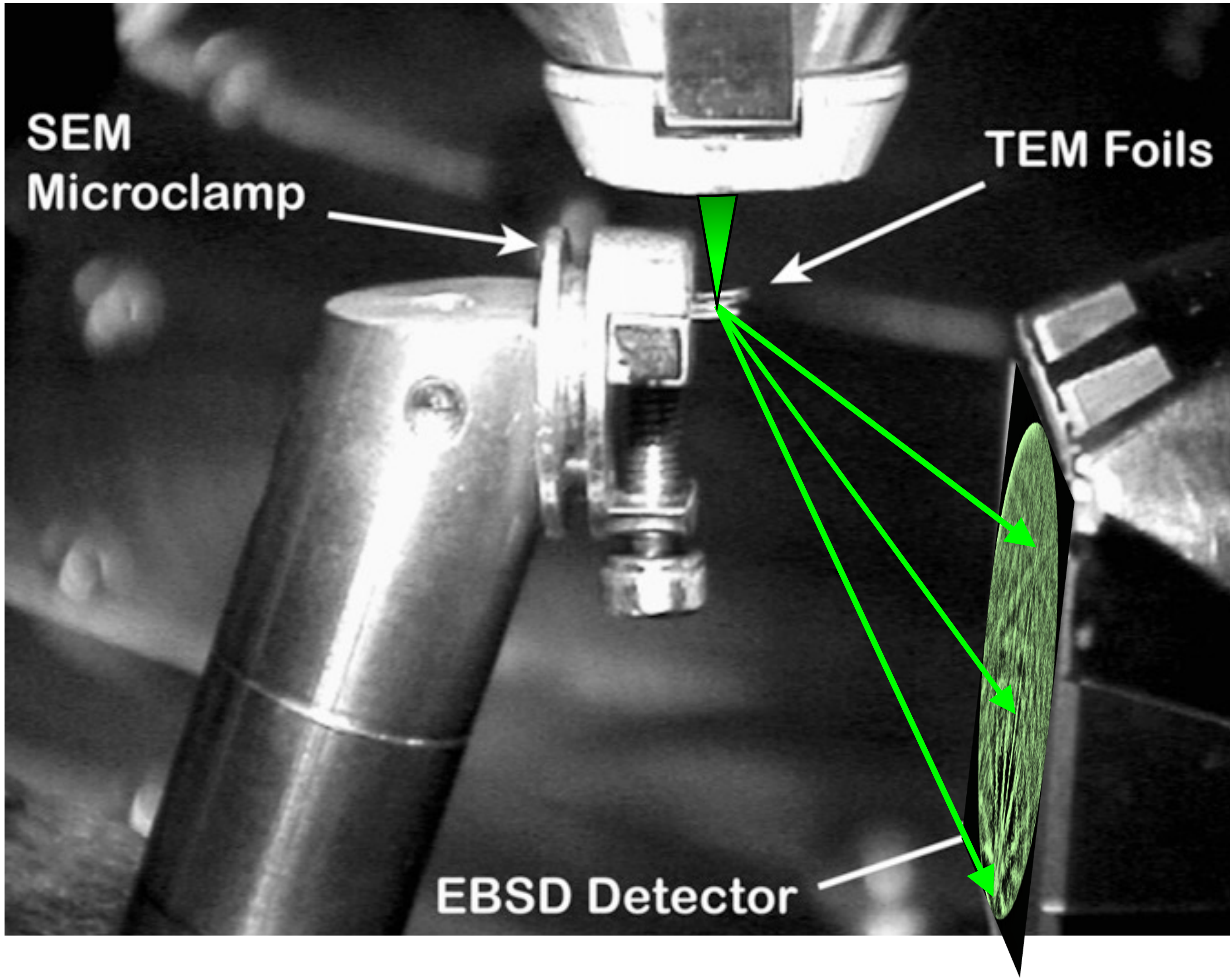
- Scanned electron probe is transmitted through a thinned sample
- Inelastically scattered electrons are diffracted off of lattice and form Kikuchi patterns in the far-field
- Spatial resolutions of about 5 nm (EBSD resolution ~150 nm)
  - Crystallographic information is from near the exit-surface only, not averaged through the sample's thickness



5. TKD: Experimental Configuration

- Samples required to be transparent at SEM beam energies (10 – 30 kV)
  - Must be >500 nm thick (actual requirement depends on through-thickness average atomic number)
  - Thinner samples yield higher spatial resolution
- Samples are commonly “back-tilted” 20° to bring more diffraction onto EBSD camera
- Short working distances are used, placing sample above the top of the EBSD camera

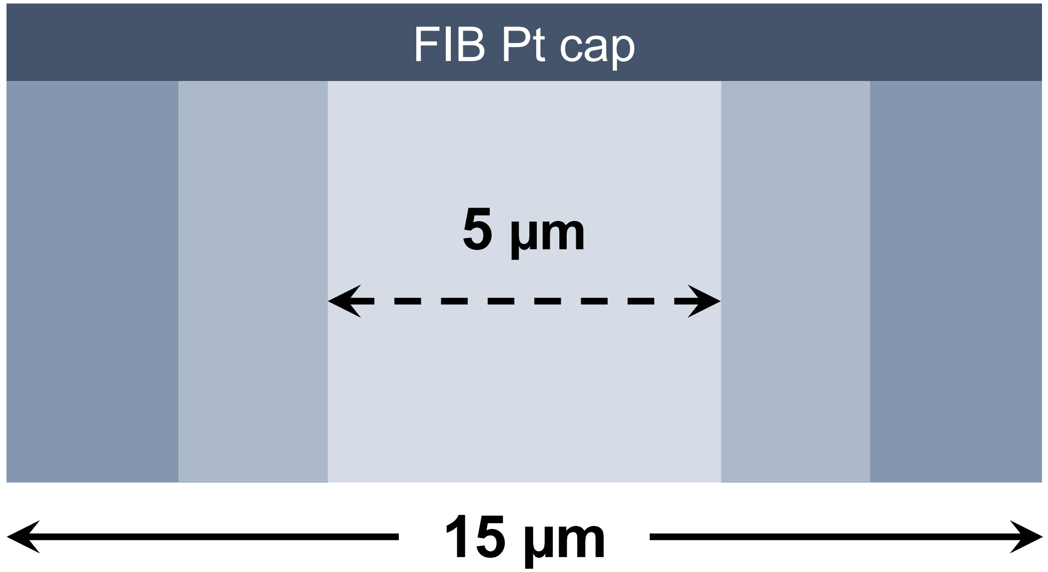
TKD setup inside the SEM

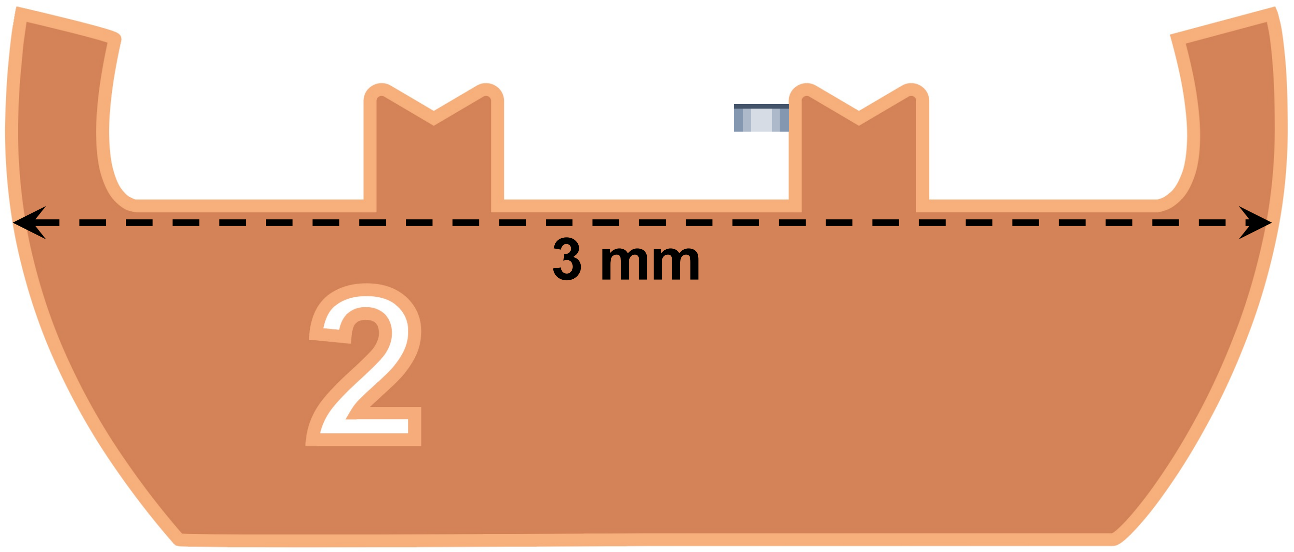


Ref: P. Trimby, Ultramicroscopy 120, 16 (2012).

5. TKD: Sample Preparation

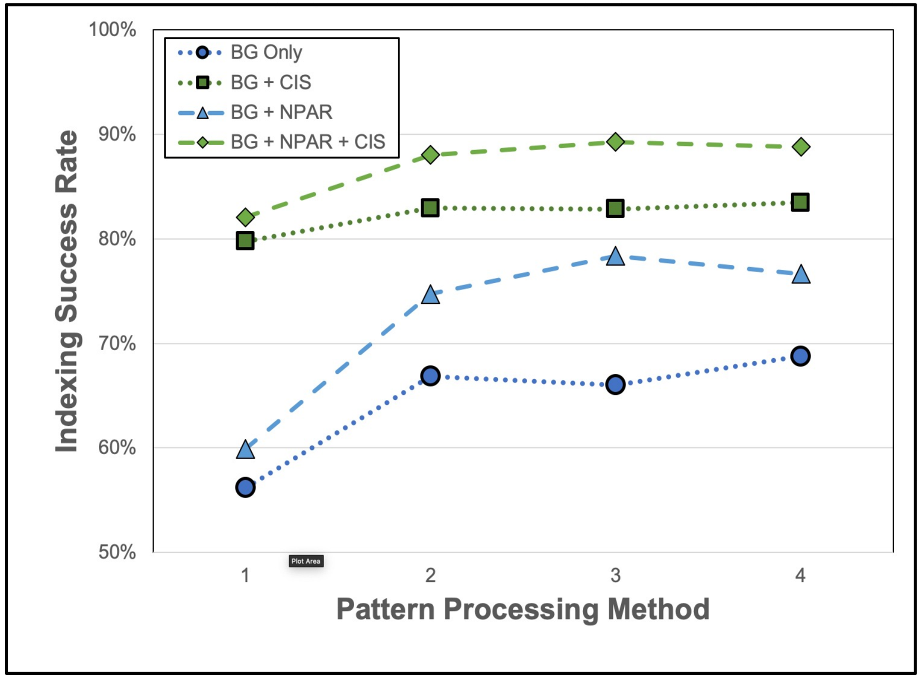
- Site-specific TKD sample prep:
  - FIB used to pull lamella from selected region of bulk sample
  - Sample mounted on TEM half-grid for TKD characterization in the SEM
  - 2 kV final polish greatly improves quality of TKD patterns
- Non-site-specific TKD sample prep:
  - Dimple-grinding and ion-milling
  - Twin-jet electropolishing
  - Wedge-polishing

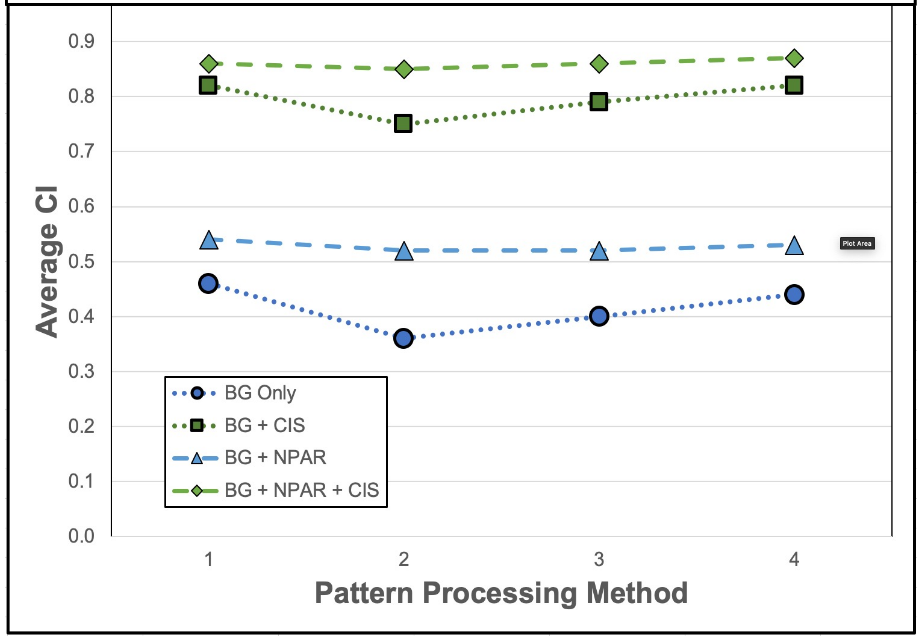


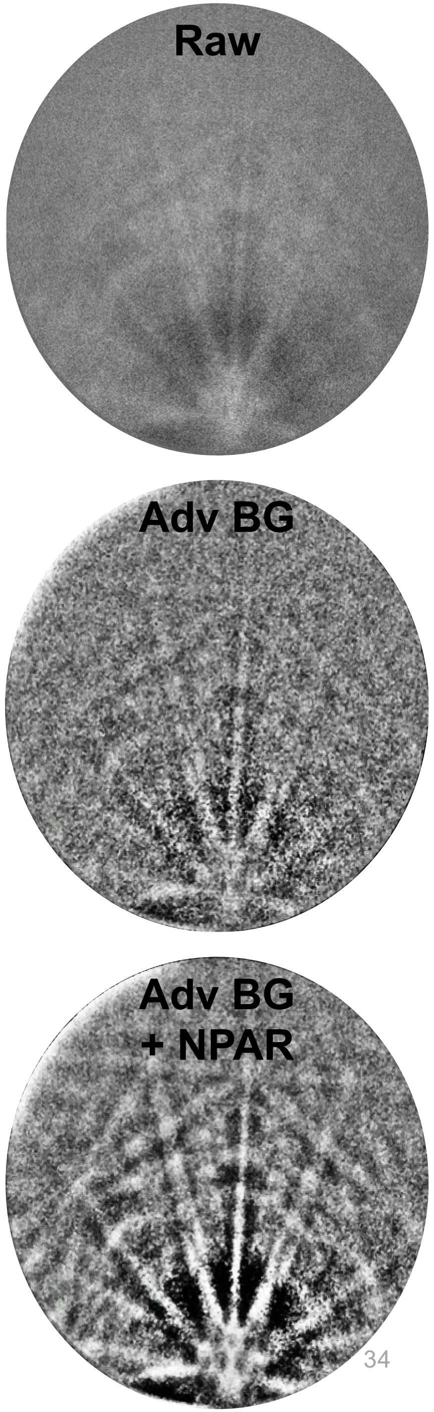


5. TKD: Data Post-Processing

- TKD data is harder to process using the traditional EBSD pipeline; local variations in sample thickness can strongly affect the background
  - Post-processing of TKD patterns making use of advanced background models and other image processing techniques yield higher quality orientation data
  - Combining and averaging each pattern with its first-nearest-neighbors yields a 1/sqrt(7) improvement in signal to noise (*i.e.* EDAX's NPAR)



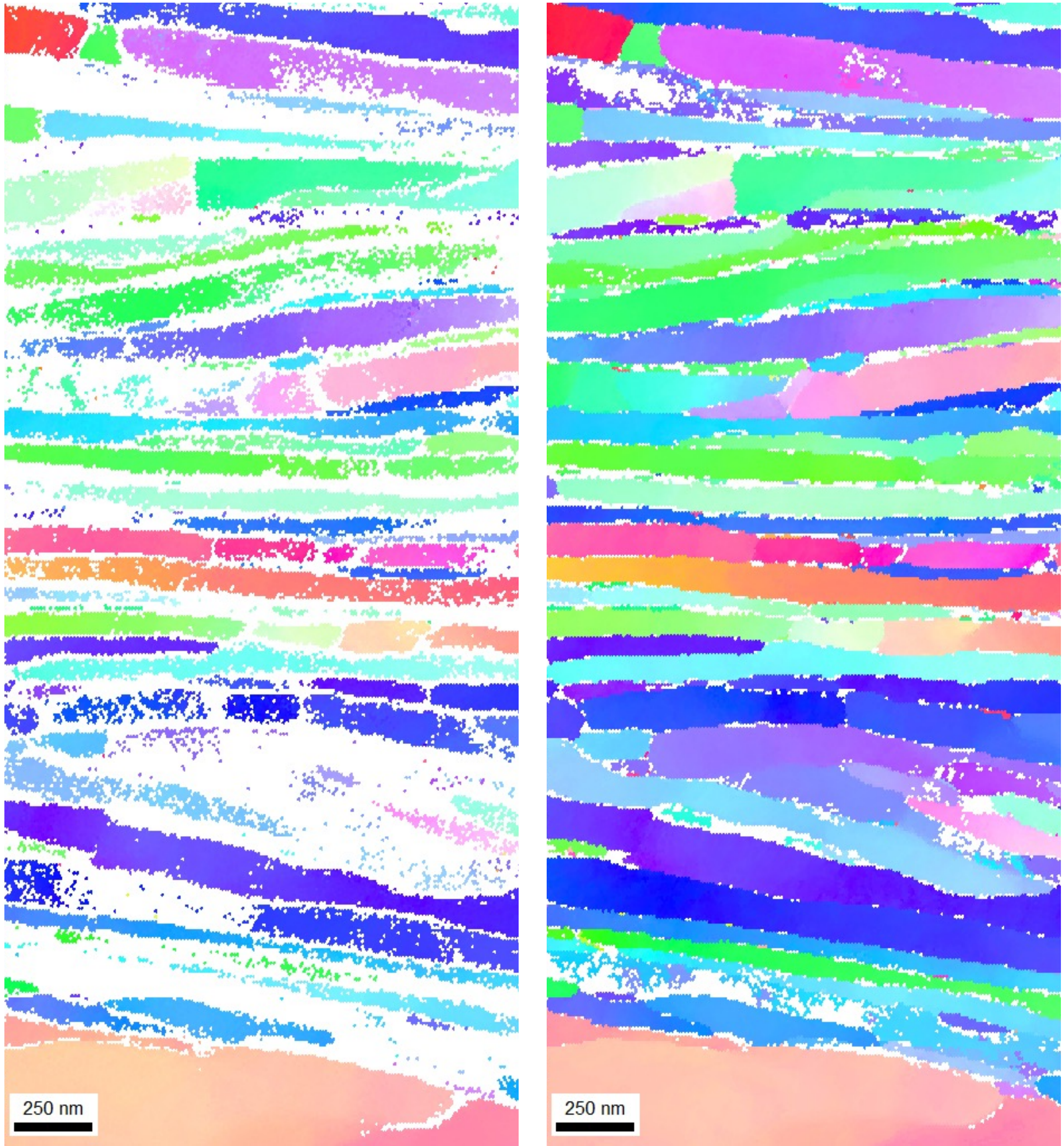




Los Alamos
NATIONAL LABORATORY

5. TKD: Post-processed Experimental Results

- Sample: Cu-Nb, 140 nm nominal layer thickness
- IPFs from static background subtraction (left) vs. advanced background processing coupled with nearest-neighbor averaging (right)
  - 38% improvement in the number of points successfully indexed



Los Alamos NATIONAL LABORATORY

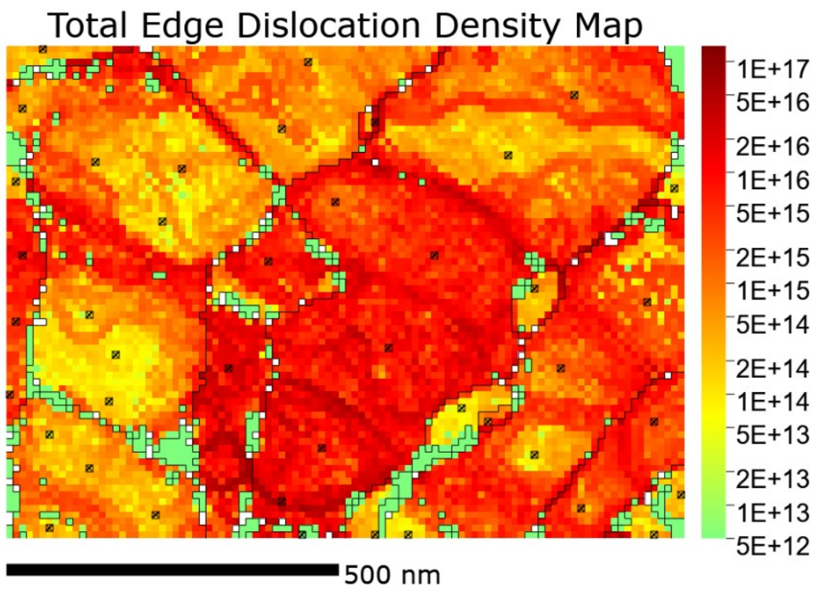
Collaborators: R. McCabe, Y. Zhang

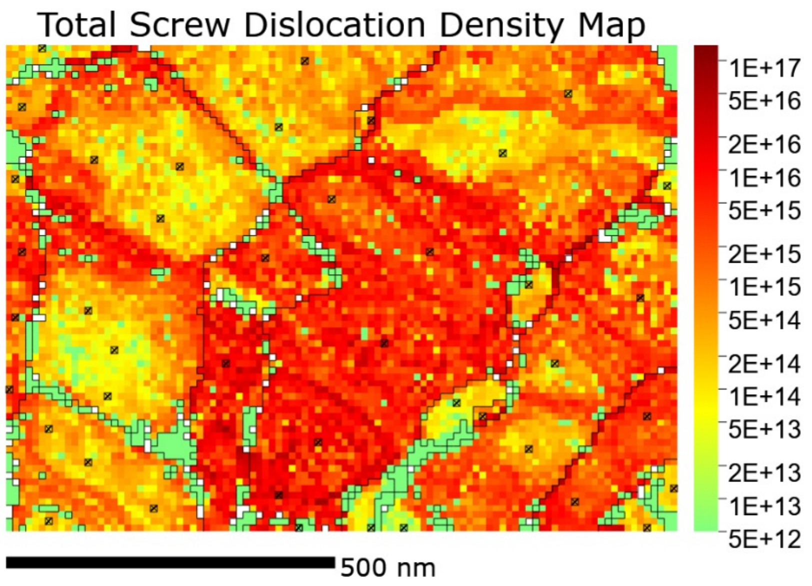
5. TKD: Technique's Current Status at the EML

- Status: Ready for use
  - Several EML users are already collecting high-quality TKD data
- Challenges: Minor
  - Data processing requires above average computational resources
  - Large datasets are common (10's to 100's of GBs)
- Prospects for future development: Good
  - Reasonably mature new technique, based on tried-and-true EBSD principles
  - Correlative workflows are improving and aiding researchers to efficiently bridge the SEM and TEM length-scales

6. SEM: HR-EBSD

- High-resolution electron backscatter diffraction (HR-EBSD) is a technique for mapping localized lattice distortions and misorientations in crystalline materials
- ”High-resolution” refers to the angular resolution to which the crystal structure can be accurately indexed





Data courtesy of Y. Zhang

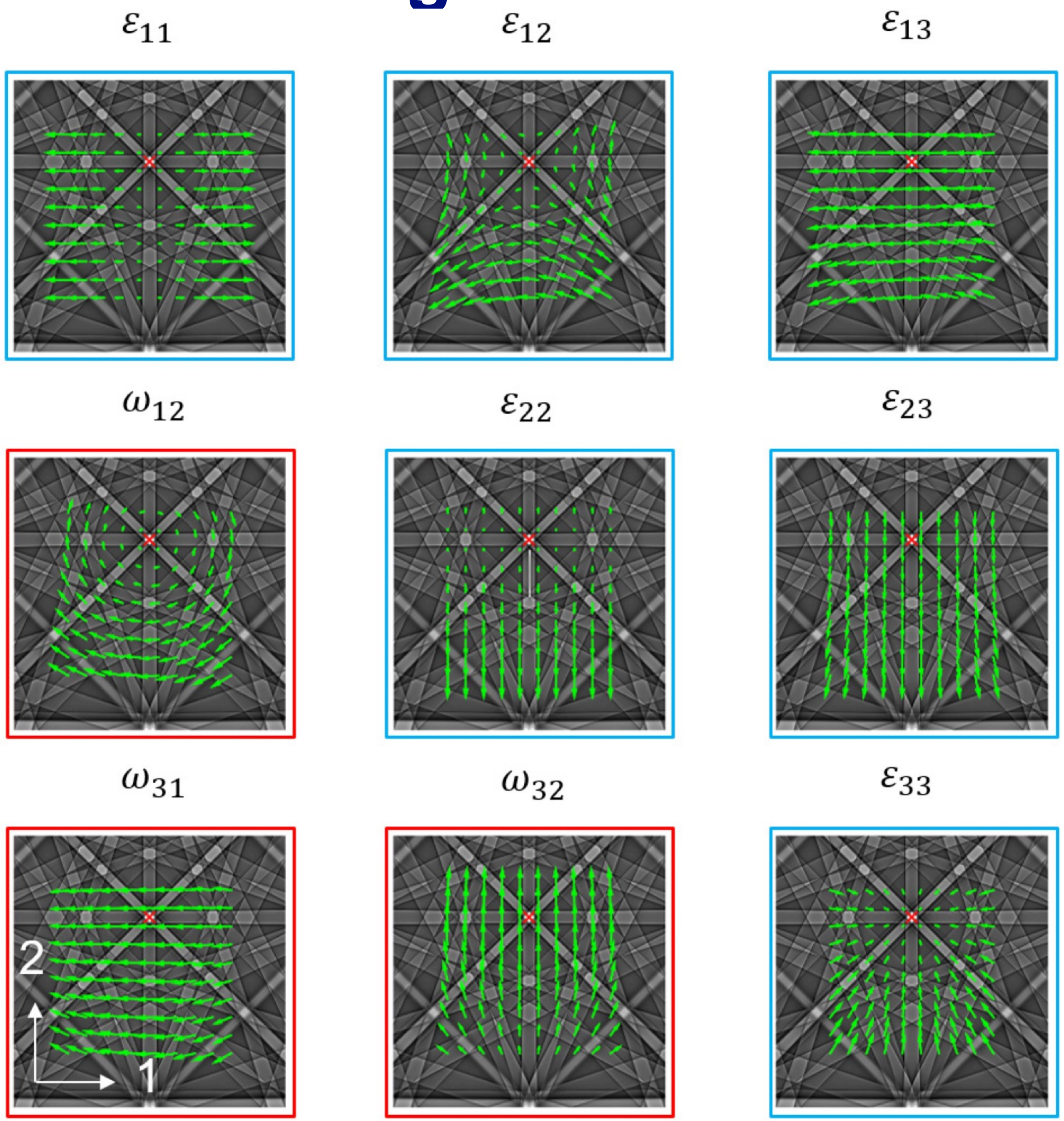
6. HR-EBSD: Conventional EBSD vs. High Res.

- **Convention EBSD**
  - Stage tilted +70°, towards EBSD camera
  - Camera setup for high-speed capture: low exposure, high-gain, single frame, binned 4x4
  - Data processing is done via Hough transform, able to process on the fly
    - Data reduction accomplished by only saving the location of Hough peaks rather than full pattern
  - **Results**:
    - Absolute orientation precision: ±2°
    - Misorientation precision: ±0.5°

- **High-Resolution EBSD**
  - Stage titled +70°, towards EBSD camera
  - Camera setup for maximum SNR: low gain, long exposure, frame averaging, un-binned
  - Data processing is conducted by cross-correlating experimentally recorded patterns versus reference patterns
    - Reference patterns from un-strained region or computed from known crystallography
  - **Results**:
    - Absolute orientation: computed conventionally
    - Misorientation precision: ±0.0006°

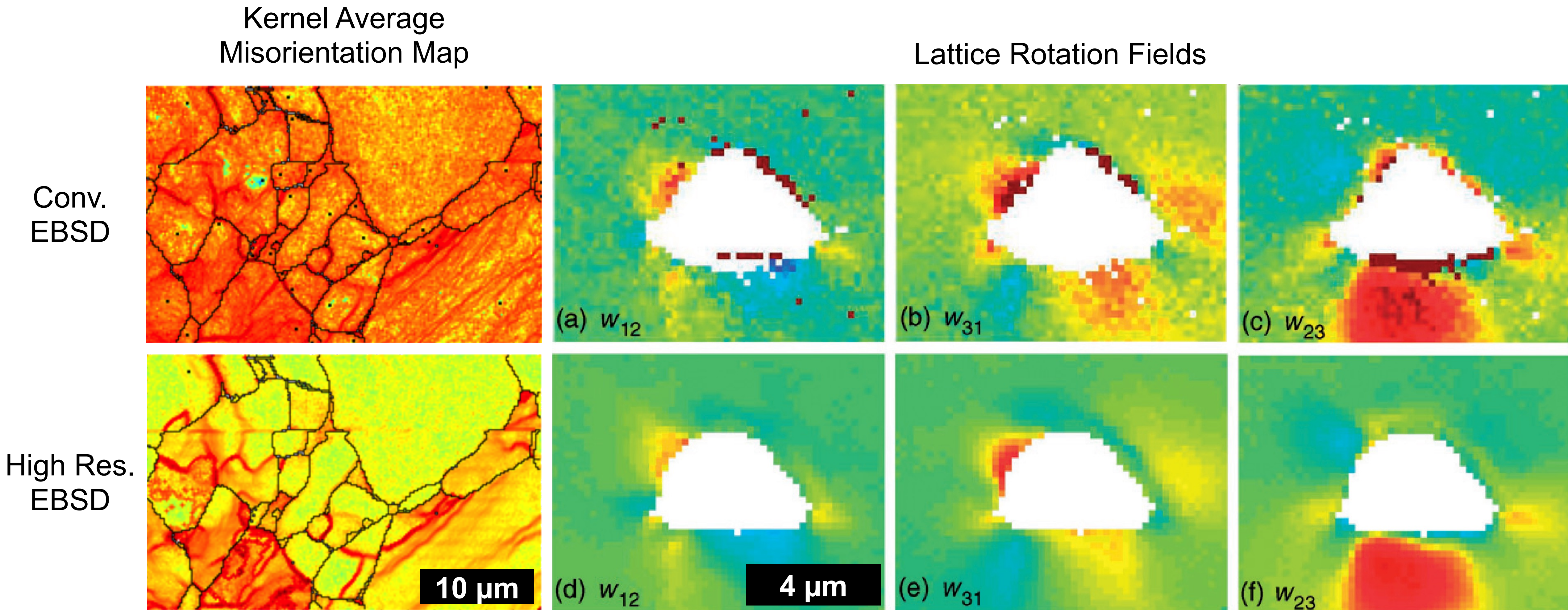
6. HR-EBSD: Cross-Correlation Processing

- Computed patterns provide ground-truth, experimentally recorded reference patterns are subject to SNR limits as well any residual strain in the sample
- Cross-correlation used to measure shifts in both zone axis location as well as rotational orientation with sub-pixel precision
- The measured shifts are directly, geometrically linked to strains and lattice rotations
- Deviations in interplanar angles and lattice orientations subsequently measured precisely and accurately



Ref: T. Britton et al., IOP Conf.: Mat. Sci. & Eng. 304 (2018).

6. HR-EBSD: Results of Conventional EBSD vs. High Res.



http://www.hrebsd.com/

Ref: A. Wilkinson & D. Randman, Phil. Mag. 90 1159 (2010).

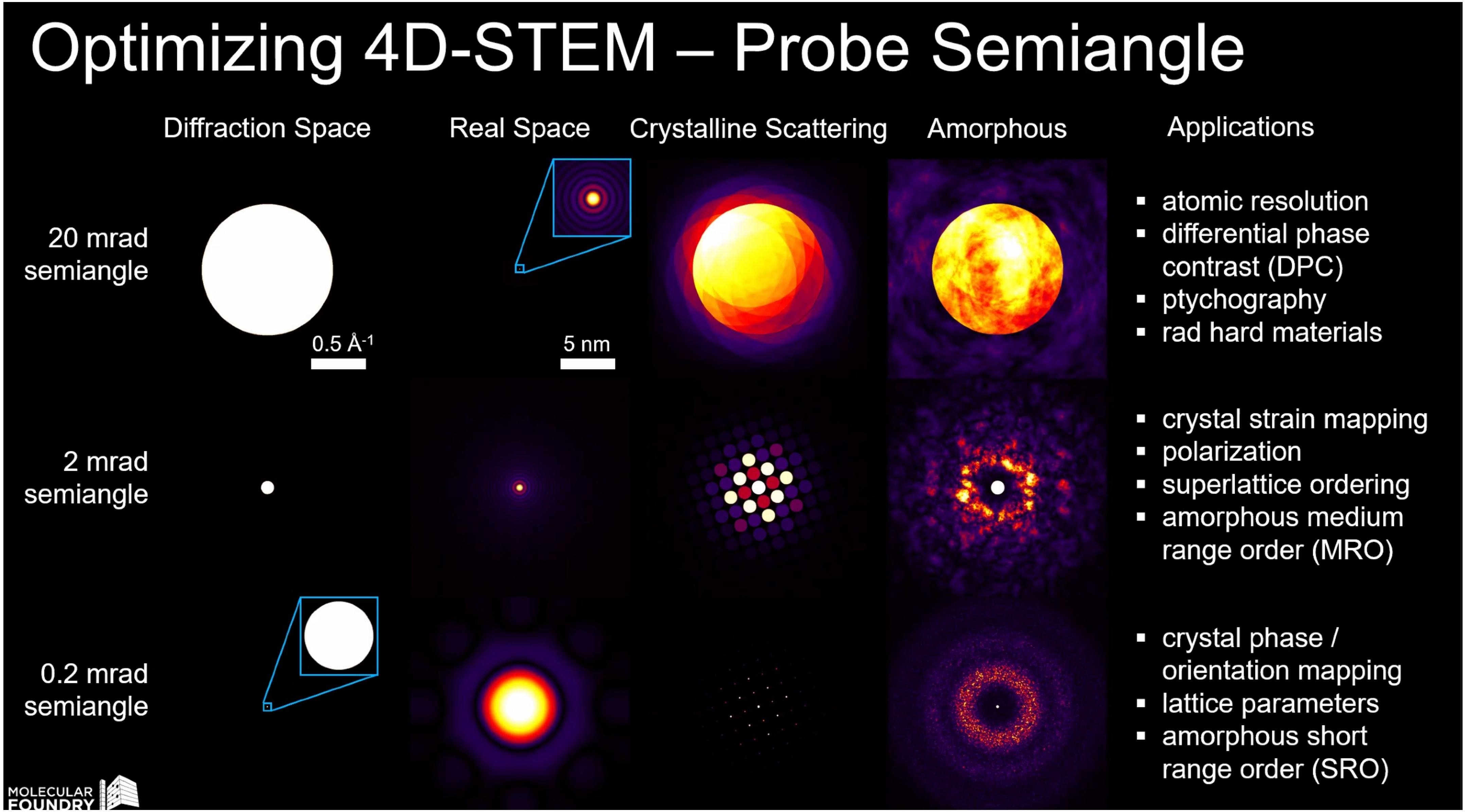
6. HR-EBSD: Technique's Current Status at the EML

- Status: Just getting started
  - Prototype datasets have been collected, these have demonstrated the limitations of current EML hardware
- Challenges: Moderate
  - Data processing requires above average computational resources
  - Large datasets are common (10's to 100's of GBs)
  - EML's current EBSD cameras are not well suited to HR collection needs
- Prospects for future development: Good
  - New EBSD camera well suited to the technique has been ordered
  - The leading commercial HR-EBSD data processing solution, Cross-Court, is already running in the EML and available for users
  - Lack of results, to date, is primarily due to lack of suitable data

Thank You

- And many thanks to collaborators:
  - Rod McCabe
  - Ben Morrow
  - Matt Janish
  - Ben Derby
  - Hi Vo
  - Michael Pettes
  - Alejandra Londoño-Calderon
  - Laurent Capolungo
  - Terry Holesinger
  - Eric Tegtmeier
  - Andrew Richards
  - Yifan Zhang
  - Nan Li
  - Many more….

Backup Slides



Shamelessly stolen from Colin Ophus, NCEM